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CONTRIBUTIONS TO THE STUDY OF RUTHENIUM, IV.[1]

THE CHLORIDES.

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IN his early work upon ruthenium, Claus described two classes of chlorides, $Ru^{III}Cl_3,2XCl$, and $Ru^{IV}Cl_4,2XCl$, corresponding to two of the general types among the metals of the platinum group; the former made by the action of hydrochloric acid upon any of the soluble oxides or hydrated oxides, the latter, generally at least, by oxidation with nitric acid. The trichloride is formed also when chlorine acts directly upon the metal, especially in the presence of alkaline chlorides.

In addition to these chlorides, Claus called attention to the fact that by the action of hydrogen sulphide, the deep red-brown solution of ruthenium trichloride becomes dark azure-blue, probably owing to reduction to a bichloride, $Ru^{II}Cl_2$. No further advance was made on the chlorides till A. Joly[2] showed that the chloride obtained by oxidation with nitric acid is not as Claus had supposed the tetrachloride, but a nitrosochloride, $RuCl_3NO$. More recently U. Antony[3] has shown that by adding potassium

[1] Read in abstract at Denver meeting of the American Chemical Society.

[2] *Compt. rend.*, **107**, 994 (1888); **108**, 854 (1889).

[3] *Gazz. chim. ital.*, **29**, 1 (1889).

ruthenate, K_2RuO_4, to hydrochloric acid, the true tetrachloride, $Ru^{IV}Cl_4,2KCl$, is really formed, and it appears quite possible that Claus may have had this salt in hand, and in one case have analyzed it. He did not at all events distinguish it from the nitrosochloride. Joly[1] also studied the azure-blue solution of the reduced chloride and concluded that it contains an oxychloride, $RuCl_3OH$.

The nitrosochloride series of salts has been quite fully worked out by Joly,[2] Brizard,[3] and the author.[4] The present paper extends the trichloride series of Claus and the tetrachloride series of Antony, to some of the cesium and rubidium members, and presents two members of a new series, $RuO_2Cl_2,2XCl$, an oxychloride intermediate between the tetroxide and tetrachloride. A few notes are appended on the blue solution.

Ruthenium Tetrachloride.—When hydrochloric acid, or free or nascent chlorine, acts upon ruthenium compounds, in almost every case, the trichloride is the resultant product. Joly, as well as the author, tried in vain, by various methods of chlorination, to form the tetrachloride. Apparently $RuCl_3$ will not take up another atom of chlorine. Antony first wittingly prepared the chloride, using potassium chlorate to oxidize the ruthenium to ruthenate, thus insuring the absence of a nitrate and hence of nitrosochloride formation. The solution of the ruthenate was then added to dilute hydrochloric acid. On the other hand, when the acid is added to the ruthenate, even at a temperature below zero, and the solution concentrated in the cold, the trichloride is the only product I have been able to obtain. The study of the conditions of formation of the tetrachloride are much enhanced in difficulty by the close resemblance of its solutions to those of the trichloride. I have as yet noted but a single analytical reaction in which the two compounds differ sufficiently to be readily distinguished, and this reaction demands the dry salt free from acid and in a fairly pure state; nor is it easy, even by the microscope, to distinguish the presence of the tetrachloride in a mixture.

The starting point of the work of the present paper was generally ruthenium tetroxide, RuO_4, distilled from the alkaline ruthenate solution by a current of chlorine. In the earlier part of

[1] *Compt. rend.*, **114**, 291 (1892).
[2] *Loc. cit.*
[3] *Bul. Soc. Chim.* [3] **13**. 1092 (1895); *Compt. rend.*, **122**, 730 (1896).
[4] This Journal, **16**, 388 (1894).

my work, the ruthenate was formed by fusing metallic ruthenium, or ruthenium residues of any kind (which must be free from osmium) with caustic potash and saltpeter, in a silver dish. The introduction of sodium peroxide into the laboratory has occasioned much economy of time and trouble in this operation. The ruthenium, in any finely divided form, is slightly mixed in a nickel dish with three or four times its volume of sodium peroxide and warmed with occasional stirring till it becomes nearly but not quite completely fused. The conversion into sodium ruthenate is rapid and generally complete, and the melt is readily soluble in a small quantity of water. To avoid undue heating, it is well to rest the nickel dish in a beaker full of cold water, or on a piece of ice, while dissolving the melt. The strong solution of the ruthenate is poured into a small tubulated retort, and through it is passed a fairly rapid current of chlorine. As the solution becomes saturated, the ruthenium tetroxide begins to pass off as a golden yellow vapor, and may be completely removed from the solution by gently warming and finally bringing to a boil. When it is desired merely to obtain a pure ruthenium, the tetroxide may be led directly into dilute alcoholic potash, but when the pure tetroxide is desired, an adapter is arranged leading into a large, stoppered test-tube, and from this any uncondensed tetroxide together with the chlorine is led into an aqueous solution of potash. Beyond the potash bottle may be placed a bottle of alcoholic potash, which will effectually retain every trace of ruthenium. Before the introduction of the aqueous potash bottle, it was found that the vapors of alcohol diffused slightly into the tetroxide tube, causing decomposition. In one instance owing to the stopping of the chlorine current a little of the alcoholic potash was drawn over into the tube, which then contained perhaps 3 or 4 grams of the tetroxide. A very violent explosion occurred which shattered the apparatus, and filled the room with dense black smoke. This ruthenium soot, evidently an oxide, differs from any described anhydrous oxide, in being very soluble in dilute hydrochloric acid. The trichloride is formed.

If the absence of osmium be assured, this method of preparing the tetroxide or of purifying ruthenium is very satisfactory, being fairly expeditious and without danger. The fumes of ruthenium tetroxide, though somewhat suffocating, appear to have the

irritating and poisonous qualities of the osmium tetroxide to a very slight degree if at all.

When ruthenium tetroxide is treated with hydrochloric acid in the cold, it is slightly soluble to a light reddish yellow solution. On standing, or on warming, the solution becomes dark red and chlorine is evolved. The rapidity of this change is proportional to the strength of the acid, and to the temperature. In five times normal acid, at ordinary temperature, some unchanged RuO_4 is present in the solution after standing several days. The primary product obtained on treating the dark red solution with an alkaline chloride is the trichloride, of formula $Ru^{III}Cl_3 2XCl$ generally at least with one molecule of water, and until recently no other compounds have been recognized.

If, however, ruthenium tetroxide is covered with water, in which it is but slightly soluble, a strong solution of cesium (or rubidium) chloride added, and the whole acidified with a small amount of hydrochloric acid, the tetroxide is gradually converted into the double salt of the oxychlorruthenate to be described in the next paragraph. This salt on boiling with concentrated hydrochloric acid is converted into the double salt of ruthenium tetrachloride, but some of the trichloride seems to be formed at the same time. Many efforts were made to obtain the tetrachloride directly from the tetroxide, but the exact conditions of the reaction were not found; the tetrachloride, however, not seldom appeared in the products. The best specimen obtained (analysis 3) was the second crop of crystals from evaporating the filtrate from the precipitation by alcohol of the reaction products of the tetroxide, cesium chloride, and concentrated acid. The previous crop had consisted of a mixture of the tetrachloride, and a rose salt to be mentioned later. Cesium and rubidium chlorruthenates, $Cs_2Ru^{IV}Cl_6$ and $Rb_2Ru^{IV}Cl_6$, when well crystallized, consist of black, almost opaque, regular octahedra, resembling the corresponding salt of the other platinum metals; when precipitated from solutions by alcohol, they are buff powders, hardly distinguishable as crystalline. They are almost insoluble in cold water, barely tinting the water brown; on heating, the solution becomes darker and slightly purplish, the salt being decomposed. If now a drop of concentrated hydrochloric acid is added, a deep purple color is noticeable in the brown solution, but it soon disappears, leaving the solution brownish. This reaction, which is very sat-

isfactory if the salt is quite pure, is the only one yet found which differentiates clearly the tetrachloride from the trichloride. The tetrachloride is less soluble in concentrated hydrochloric acid than the trichloride; is fairly soluble in hot dilute hydrochloric acid. The solution in hydrochloric acid resembles that of the trichloride, save for a slight cast of pink to the deep red concentrated solutions, and a pure yellow in dilute solutions, as against the reddish cast to the yellow of the trichloride.

The alkalies give a dull greenish blue precipitate (or color only with ammonia); with all other reagents tested, the reactions in no wise differed from those of the salts of ruthenium trichloride. When acidified with hydrochloric acid and boiled in dilute solution, especially with alcohol, the solution becomes rose, and on slow evaporation the rose prisms described later are found together with the octahedra of the unchanged tetrachloride.

Cesium and Rubidium Oxychlorruthenate, $Cs_2RuO_2Cl_4$ and $Rb_2RuO_2Cl_4$ ($2CsCl,RuO_2Cl_2$, and $2RbCl,RuO_2Cl_2$).—These salts are slowly formed by the action of a solution containing little hydrochloric acid and much alkaline chloride, on excess of ruthenium tetroxide, in the cold. Owing to the volatility of the tetroxide and its instability, especially in the presence of any organic vapors, the best method of preparing the salt was found to be as follows: Two or three grams of ruthenium tetroxide (more or less water is in the distillate used) were poured into a glass weighing-tube of 3 cm. diameter. A few cubic centimeters of a quite concentrated solution of cesium (or rubidium) chloride were added and a few drops of concentrated hydrochloric acid. The tube is then stoppered and shaken from time to time. The stopper must be occasionally removed to permit the escape of the chlorine generated. In the course of twenty-four hours, a considerable crop of the crystals of the salt may be removed, dried on a tile, and after the volatilization of the ruthenium tetroxide which will be present, the salt may be washed by a trace of hydrochloric acid. Successive crops may be obtained. These salts consist of dark purple isometric crystals, showing the octahedron, cube, and rhombic dodecahedron. They are quite soluble in cold hydrochloric acid to rose solution, yellow on dilution; from *cold* solution, the salt crystallizes out unchanged, even in the presence of alcohol.

On heating with hydrochloric acid, chlorine is evolved and the

corresponding salt of ruthenium tetrachloride crystallizes out.

The characteristic reaction of the oxychlorruthenate is its instant decomposition by water. When even a very small crystal is let fall into a drop of water on a watch-glass, it at once dissolves and decomposes, rendering the whole drop a black liquid. At the same time there is noticeable a marked odor of ruthenium tetroxide. The salt is also decomposed by sulphuric and nitric acids with the evolution of the same odor.

These two salts belong to a type with very few representatives. Péligot by the action of hydrochloric acid on potassium uranate obtained $2KCl,UO_2Cl_2.2H_2O$, and Sendtner prepared the corresponding bromide.

By the action of hydrofluoric acid on potassium tungstate, Berzelius obtained $2KF,WO_2F_2.H_2O$ and two or three other analogous tungstates. The chlorotungstate WO_2Cl_2, like the corresponding MoO_2Cl_2 and CrO_2Cl_2, exhibits no tendency to form salts. Piccini's ammonium fluotitanate, $3NH_4F,TiO_2F_2$, seems rather of the nature of a peroxide.

The uniform nature of the oxychlorruthenate was evident under the microscope, before and after recrystallization. The absence of water or of hydroxyl groups in the salt was shown by heating in oxygen stream in a tube guarded at either end with a phosphorus pentoxide tube (see Analysis 9). This shuts out the possibility of the salt being $Ru(OH)_2Cl_2$. The formation of the salt and its decomposition with hydrochloric acid are shown by the formulas:

(*a*) $RuO_4 + 4HCl + 2CsCl = 2CsCl,RuO_2Cl_2 + 2H_2O + Cl_2$.

(*b*) $2CsCl,RuO_2Cl_2 + 4HCl = 2CsCl,RuCl_4 + 2H_2O + Cl_2$.

The odor of ruthenium tetroxide, when the salt is decomposed by water or other acids than hydrochloric, may be the odor of ozone, the formation of which would be readily explicable. When ruthenium tetroxide comes in contact with any organic substance it is instantly decomposed, and it may well be that the oxide is decomposed before stimulating the olfactory nerves, and the odor recognized is that of ozone, formed by the decomposition of the oxide. At least the two odors resemble each other very closely.

Ruthenium Trichloride Salts.—The salts of the lighter alkali metals have been fully described by Claus and Joly. Cesium and rubidium chlorides show the familiar tendency to form complex

salts with ruthenium trichloride, according to the conditions of experiment. The normal salts are $Cs_2RuCl_5.H_2O$ and $Rb_2RuCl_5.H_2O$, the presence of the water of crystallization being confirmed by Analyses 13 and 17. The water is slowly driven off by heat and at 250° one atom of chlorine is very slowly lost.

Indications of more complex salts were obtained and several analyses of these are appended. In most of these cases there is no assurance that the salt, always difficult to dry, was pure or uniform (except 21), but the fact that salts of approximately the same composition were obtained from different sources, points to the probability that they are definite compounds.

One salt, however, of this class is characterized by forming uniform, transparent, rose prisms, with extinction parallel to the prism. These are deposited from the rose solution obtained when a slightly acid solution of the tetrachloride is heated with considerable excess of water and alcohol. It is also deposited from the filtrate after the electrolytic reduction of the trichloride. It is also probably formed in dilute solutions of the trichloride, but it has not been analyzed, nor positively identified from this source. It is not very soluble in hydrochloric acid, and is very slightly soluble in water. It can be crystallized apparently unchanged from hydrochloric acid, but on evaporating to dryness in hydrochloric acid solution, some tetrachloride is formed. The composition of these rose prisms is $Cs_2RuCl_5.H_2O$, the same as that of the normal cesium salt of the trichloride, but they are very distinct from that salt, and should probably be looked upon as an *aquo* salt, $2CsCl,Ru(OH_2)Cl_3$, corresponding to the tetrachloride, $2CsCl,RuCl_4$.

Ruthenium Dichloride (?).—Forty years before the discovery of ruthenium by Claus, Vanquelin had noticed the azure-blue color produced by the action of zinc upon certain solutions, a reaction which he attributed to osmium. One of the most characteristic reactions of trivalent ruthenium is this blue color formed by the action of hydrogen sulphide. Since it is produced by the action of reducing agents upon the solution of ruthenium trichloride, Claus attributed it to the formation of a bichloride, but he did not separate the salt. When a mixture of chlorine and carbon monoxide is passed over finely divided ruthenium at a comparatively low temperature, a very voluminous powder is obtained which contains anhydrous trichloride, as shown by Joly. This

is insoluble in water, acids, and strong alcohol, but is freely soluble in dilute alcohol, to the same dark azure-blue solution. On distilling the solution in vacuum, Joly obtained what he considered to be an oxychloride, and he looked upon the blue solution as $Ru(OH)Cl_2$. Inasmuch as in the solution of this variety of the trichloride, aldehyde is formed, and since the blue color is produced in every case by a reducing action, it seems to me probable, that a true bichloride is present. In spite of much effort, I have not succeeded in preparing a pure salt from the blue solution, but several that have been prepared point to a compound of the formula $3CsCl,2RuCl_2.2H_2O$. These were formed by reducing a solution of ruthenium trichloride in an electrolytic cell, and immediately adding a solution of cesium or rubidium chloride. The fine precipitate varies from dark greenish blue to olive-green, oxidizes with great rapidity, and is very difficult to filter and wash, even under suction. Analyses of a number of the precipitates are given, two of which, 24 and 25, point to the above formula. In the others the amount of chlorine is too large in proportion to the ruthenium for $RuCl_2$, though in every case less than is required for $RuCl_3$. The addition of cesium chloride to the blue alcoholic solution of the anhydrous trichloride causes a precipitate much resembling that from the solution obtained by electrolytic reduction, but it has not yet been found possible to filter it off and wash it. The investigations upon the blue solution are still being carried on.

Another investigation now in progress may also be mentioned in this connection. An attempt was made to reduce the trichloride of ruthenium by stannous chloride. If the salt is not completely in solution a fugitive greenish blue solution is produced, but in general the dark yellowish red solution of the trichloride becomes much lighter, and if dilute, is almost completely decolorized. On adding water to this solution a yellow flocculent precipitate is formed, which contains all the ruthenium which was in the solution. This precipitate is insoluble in hot water, but easily soluble in hydrochloric acid, from which it is again precipitated on dilution. From the hydrochloric acid solutions are obtained two crystalline salts: one consists of white to pale yellow octahedra of cesium (or rubidium) chlorostannate, thus showing an oxidation of the tin; the other crystals are brilliant red (apparently) octahedra. These seem to be perfectly uniform

and analysis shows them to contain both tin and ruthenium.

For the material used in my work, I am indebted to Johnson, Matthey and Co., of London, for crude ruthenium; to Baker & Co., of Newark, N. J., for the use of several ounces of iridosmium; and to the Imperial Academy of Sciences, through its president and Professor N. N. Beketoff, director of its laboratory, for a considerable quantity of ruthenium.

ANALYTICAL WORK.

The analysis of most of the salts described in this paper was carried out by heating 0.2 to 0.35 gram of the salt contained in a platinum or at times in a porcelain boat, in a combustion tube in a current of hydrogen. The hydrochloric acid evolved was collected in a solution of silver nitrate, guarded by a second silver nitrate solution, to prove complete absorption of the gas. This gave the chlorine freed from the ruthenium by heat. The residue, consisting of ruthenium and alkali chloride, was extracted with hot water, followed by dilute acid. The alkali chloride was then determined, either by evaporation or by precipitation of the chlorine. The ruthenium was heated in a hydrogen stream before weighing; occasionally the ruthenium, on being brought to the air, glowed, and was slightly oxidized, giving results a little too high.

For the direct determination of water, or hydroxyl groups, the salt was heated in oxygen in a porcelain boat, and several coils of silver foil kept in front of the boat. The rear end of the combustion tube was guarded by a phosphorus pentoxide tube, and the gas from the tube passed through a weighed phosphorus pentoxide tube. The chlorine given off in the oxygen stream was almost completely held by the first silver coil. After heating in oxygen, the phosphorus pentoxide tube was removed, silver nitrate solution substituted, and the analysis continued in a hydrogen stream in the usual way. The only defect of this method is that, even at the low heat used, a small quantity of ruthenium is volatilized in the oxygen; hence, where this method was used the ruthenium is a little low.

Cesium Chlorruthenate, Cs_2RuCl_6.—Dark brown to black powder; under the microscope black octahedra; larger crystals are dark purplish red by transmitted light. It is almost insoluble in water, very slightly soluble in hydrochloric acid. It is best dissolved in

hot dilute hydrochloric acid, giving a reddish yellow solution, a decided yellow on dilution. The aqueous solution somewhat decomposed on boiling. The usual ruthenium reactions were given with potassium thiocyanate, and with ammonia and thiosulphate. The purple of this latter reaction comes more quickly than with the trichloride salts.

1. Filtrates from $Cs_2RuO_2Cl_4$ (formed from RuO_4, CsCl, and HCl), boiled with hydrochloric acid, precipitated by alcohol as buff powder and recrystallized from hydrochloric acid, 0.2171 gram.

2. The alcoholic filtrate (similar to 1) evaporated somewhat giving on cooling black and red ($Cs_2Ru(OH_2)Cl_5$) crystals, extracted with warm hydrochloric acid in which red crystals are more soluble, 0.4220 gram.

3. From 2 by further evaporation. Resembles black sand, 0.6118 gram.

4. From $Cs_2Ru(OH_2)Cl_5$ (rose prisms) by boiling with concentrated hydrochloric acid. Contains small amount of trichloride, 0.2038 gram.

	1.	2.	3.	4.	Theory.
Ruthenium	17.69	17.94	17.64	....	17.51
Chlorine (with ruthenium)	23.76	22.54	24.05	22.11	24.44
Cesium	46.63	46.00	45.59	....	45.82
Chlorine (with cesium)	12.42	12.27	12.16	....	12.22

Rubidium Chlorruthenate, Rb_2RuCl_6.—Octahedra, similar to the cesium salt.

5. Crystallized out of evaporated alcoholic filtrate from precipitation of salt formed by warming RuO_4 with RbCl and strong hydrochloric acid, 0.2914 gram.

	5.	Theory.
Ruthenium	21.20	20.93
Chlorine (with ruthenium)	28.78	29.22
Rubidium	35.12	35.24
Chlorine (with rubidium)	14.99	14.61

Cesium Oxychlorruthenate, $Cs_2RuO_2Cl_4$, or $2CsCl,RuO_2Cl_2$.—Dark reddish purple powder; under microscope regular octahedra. Decomposed instantly by water, giving black precipitate. Soluble in cold hydrochloric acid to rose solution; evolves chlorine with hot hydrochloric acid; decomposed by sulphuric acid and nitric acid, giving odor of RuO_4 (O_3?); deflagrates slightly on heating. Formed by the action of cesium chloride and dilute hydrochloric acid on RuO_4 with little water.

6. First crop of crystals, 0.2955 gram.

7. Second crop, 0.3635 gram.

8. 6 and 7 mixed, 0.4538 gram.

	6.	7.	8.	Theory.
Ruthenium	20.51	21.76	18.86	18.76
Chlorine (with ruthenium)	12.91	13.72	....	13.11
Cesium	48.29	48.76	49.18	49.11
Chlorine (with cesium)	12.25	12.45	13.12	13.11
Oxygen	....	....	....	5.91

Rubidium Oxychlorruthenate, $Rb_2RuO_2Cl_4$.—Similar to cesium salt. Formed in a similar manner, except in closed vessel. Second crop of crystals, washed with hydrochloric acid.

9. Heated in oxygen with silver coils and phosphorus pentoxide tubes, 0.2843 gram.

10. Heated in hydrogen, 0.2995 gram.

	9.	10.	Theory.
Ruthenium	22.09	22.70	22.76
Chlorine (with ruthenium)	15.78	16.07	15.88
Rubidium	38.80	38.43	38.31
Chlorine (with rubidium)	16.09	15.93	15.88
Oxygen	....	6.53	7.17

In 9 the increase in weight in the phosphorus pentoxide tube was 0.0021 gram. The formula $Rb_2Ru(OH)_2Cl_4$ would have required 0.0114 gram.

In 10 the oxygen was determined by loss of weight in hydrogen less chlorine given off.

Cesium Aquochlorruthenate, $Cs_2Ru(OH_2)Cl_5$ or $2CsCl,Ru(OH_2)Cl_3$.—Rose prisms several millimeters long, no end faces, extinction parallel to edges of prism, when fine, as when precipitated by alcohol, a buff powder. Very slightly soluble in water, more soluble in hydrochloric acid to rose solution, pink on dilution. Crystallizes unchanged from solution in hydrochloric acid, but evaporated with hydrochloric acid on water-bath is partly converted into Cs_2RuCl_6.

11. Precipitated by alcohol from blue filtrate from electrolytically reduced $RuCl_3$ and CsCl; buff powder, 0.1493 gram.

12. From evaporated filtrate after partial precipitation of Cs_2RuCl_6 (Analysis 1) by alcohol. Rose prisms, 0.2636 gram.

	11.	12.	Theory.
Ruthenium	17.88	18.25	18.07
Chlorine (with ruthenium)	18.93	18.76	18.90
Cesium	47.48	46.93	47.23
Chlorine (with cesium)	12.67	12.52	12.60
Water (by loss)	2.97	3.74	3.20

Cesium Ruthenium Trichloride, $Cs_2RuCl_5.H_2O$ or $2CsCl,RuCl_3.H_2O$.—Dark brown powder; under the microscope, tables, probably orthorhombic; when thin, brown; when thicker, dark brownish red. Some crystals one or two millimeters long exhibit base, pinacoids and dome. The chemical properties are those of ordinary salts of ruthenium trichloride. Fairly soluble in water and hydrochloric acid.

13. Formed by action of RuO_4 on hydrochloric acid and addition of cesium chloride. Recrystallized from dilute hydrochloric acid. Analysis in oxygen with phosphorus pentoxide tubes, 0.4019 gram.

	13.	Theory.
Ruthenium	18.61	18.07
Chlorine (with ruthenium)	19.11	18.90
Cesium	....	47.23
Chlorine (with cesium)	....	12.60
Water (by phosphorus pentoxide)	3.28	3.20

Rubidium Ruthenium Trichloride, $Rb_2RuCl_5.H_2O$, or $2RbCl,RuCl_3.H_2O$.—Properties and formation similar to cesium salt.

14. RuO_4 treated with concentrated hydrochloric acid and RbCl cold; recrystallized from hydrochloric acid, 0.3235 gram.

15. Same method but warm hydrochloric acid; recrystallized, 0.2925 gram.

16. Same method, warm hydrochloric acid; minute brown transparent tables, not recrystallized, 0.2598 gram.

17. Same, recrystallized, analysis in oxygen with phosphorus pentoxide tubes, 0.2480 gram.

18. RuO_4 precipitated as hydrated oxide by alcoholic potash. Precipitate dissolved in hydrochloric acid and RbCl added to hot solution. Crystallized out on cooling. Heated to 260° two hours. A subsequent experiment showed that this salt continued to lose weight very slowly at 260° during upwards of a week and only becomes constant when one atom of chlorine has been given off, 0.2027 gram.

	14.	15.	16.	17.	18.	Theory.
Ruthenium	22.13	22.46	22.25	23.15	22.39	21.73
Chlorine (with ruthenium)	22.90	22.42	23.37	23.01	23.09	22.74
Rubidium	37.88	36.27	37.45	35.78	37.17	36.48
Chlorine (with rubidium)	15.71	15.66	14.45	14.83	15.41	15.19
Water	2.26[1]	3.18[1]	2.08[1]	2.66[2]	4.58[3]	3.85

[1] By difference.
[2] By phosphorus pentoxide.
[3] 3.11 at 260° + 1.47 by difference.

Complex Cesium Salts of Ruthenium Trichloride.—Analyses give evidence of the existence of a number of these salts, though the formulas cannot be considered as established, as there is no certainty that the substance analyzed was completely uniform. Analyses of three of these salts are appended.

19. Fine brown powder, precipitated by cesium chloride from a solution of RuO_4 in concentrated hydrochloric acid, 0.5496 gram.

20. Minute brown crystals precipitated by alcohol from the filtrate from 19, 0.0744 gram.

They both correspond most closely to the formula $3CsCl,2RuCl_3.3H_2O$.

	19.	20.	Theory.
Ruthenium	19.81	20.97	20.84
Chlorine (with ruthenium)	22.04	20.37	21.81
Cesium	41.63	42.74	40.91
Chlorine (with cesium)	11.10	11.43	10,90
Water (by loss)	5.37	4.09	5.54

21. Black crystals, seemingly uniform octahedra, crystallized on cooling from a strongly acid solution of hydrated oxide of ruthenium and cesium chloride in hydrochloric acid, 0.1217 gram.

Corresponds best to $3CsCl,2RuCl_3.H_2O$.

	21.	Theory.
Ruthenium	20.53	21.64
Chlorine (with ruthenium)	22.72	22.65
Cesium	42.28	42.46
Chlorine (with cesium)	11.27	11.33
Water (by loss)	1.20	1.91

22. Brown powder, on evaporation of filtrate from 12, 0.1774 gram.

23. Dark chocolate brown powder. Buff alcoholic precipitate from warmed RuO_4, CsCl, and dilute hydrochloric acid, dissolved in dilute hydrochloric acid and evaporated nearly to dryness. Deposited from hot solution during evaporation, 0.1209 gram.

22 and 23 correspond best to the formula $5CsCl,3RuCl_3.H_2O$.

	22.	23.	Theory.
Ruthenium	20.41	20.02	20.54
Chlorine (with ruthenium)	21.00	21.45	21.50
Cesium	45.46	45.45	44.79
Chlorine (with cesium)	12.12	12.12	11.94
Water (by loss)	1.01	1.38	1.21

Lower Chloride of Ruthenium, $RuCl_3$(?).—The following

analyses are given to indicate the composition of the blue solution formed on the electrolytic reduction of ruthenium trichloride. The concentrated solution was either added to a strong solution of cesium chloride, or vice versa, with or without the addition of alcohol. The precipitate was immediately filtered on a Hirsch funnel and washed with dilute hydrochloric acid and alcohol, and dried on a tile.

	24.	25.	26.	27.	28.
Ruthenium	24.16	22.40	17.30	18.56	18.02
Chlorine (with ruthenium)	16.15	16.39	17.11	17.46	15.80
Cesium	43.96	43.89	50.01	49.75	50.51
Chlorine (with cesium)	11.73	11.78	13.35	13.27	13.46
Water (by loss)	4.18	4.22	3.37	3.16	4.91
Ratio Ru : Cl (with Ru)	1:1.9	1:2.1	1:2.84	1:2.7	1:2.5
Ratio Cl(with Cs) : Cl(with Ru)	1:1.4	1:1.4	1:1.27	1:1.3	1:1.17
Weight of analysis	0.1672	0.2188	0.1289	0.1794	0.2714

	29.	30.
Ruthenium	23.43	22.23
Chlorine (with ruthenium)	21.65	21.54
Rubidium	34.02	....
Chlorine (with rubidium)	14.13	....
Water (by loss)	2.89	2.72
Ratio Ru : Cl(with Ru)	1:2.64	1:2.77
Ratio Cl(with Rb) : Cl(with Ru)	1:1.53	....
Weight of analysis	0.1626	0.2168

Except in the case of 24 and 25 there is evidently no approximation to a definite compound, the substances being varying mixtures of $2CsCl,RuCl_3.H_2O$ with a reduced chloride. 24 and 25 would indicate that the composition of this chloride is $3CsCl_2$, $2RuCl_2.H_2O$, or if Joly's supposition is correct, $3CsCl,2Ru(OH)Cl_2$. The theoretical composition of the former salt is

Ruthenium	22.93
Chlorine (with ruthenium)	16.00
Cesium	45.00
Chlorine (with cesium)	12.00
Water	4.06

but in spite of the tolerable agreement of Analyses 24 and 25, the formula cannot be considered as established, and it is hoped that by varying the conditions of its preparation, a salt of assured purity may be obtained.

WASHINGTON AND LEE UNIVERSITY, LEXINGTON, VA.
August 20, 1901.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE.]

ON α-OXYBENZYLIDENE ACETOPHENONE.

BY F. J. POND, H. J. YORK, AND B. L. MOORE.

Received August 2, 1901.

IT has been shown in a previous paper[1] that when benzylidine acetophenone dibromide, $C_{15}H_{12}O.Br_2$, is treated with sodium alcoholate, it is readily converted into a compound, $C_{15}H_{12}O_2$, which is identical in all respects with the substance long known as *dibenzoyl methane*. The latter compound was first prepared by Baeyer and Perkin[2] by boiling dibenzoyl acetic acid ester with water during several hours; it was subsequently studied by Claisen,[3] who obtained it by the action of metallic sodium or sodium ethylate upon a mixture of acetophenone and benzoic acid ester. This compound was represented as a β-diketone, having the formula

$$C_6H_5—CO—CH_2—CO—C_6H_5.$$

Almost simultaneous with the publication of the above-mentioned paper in this Journal, J. Wislicenus[4] published an article "On the Isomeric Forms of Dibenzoyl Methane." According to Wislicenus, two molecular proportions of potassium or sodium hydroxide dissolved in alcohol react with benzylidene acetophenone dibromide in accordance with the equation

$$C_{15}H_{12}O.Br_2 + 2KOH = 2KBr + H_2O + C_{15}H_{12}O_2.$$

The product, $C_{15}H_{12}O_2$, consists of a mixture of two isomeric compounds of the same melting temperature, one of which is identical with Baeyer and Perkin's, and Claisen's dibenzoyl methane; this compound is unsaturated, and Wislicenus designates it as *α-oxybenzylidene acetophenone*,

$$C_6H_5—C(OH)=CH—CO—C_6H_5.$$

The second isomeric compound, $C_{15}H_{12}O_2$, is saturated, and may prove to be the true dibenzoyl methane or, possibly, a substance having a molecule constituted like ethylene oxide,

[1] Pond, Maxwell, and Norman: This Journal, **21**, 955.
[2] Baeyer and Perkin: *Ber. d. chem. Ges.*, **16**, 2134; *J. Chem. Soc.* (London), **47**, 250.
[3] L. Claisen: *Ber. d. chem. Ges.*, **20**, 655; *Ann. Chem.* (Liebig), **291**, 52.
[4] J. Wislicenus: *Ann. Chem.* (Liebig), **308**, 219.

$C_6H_5—CO—CH_2—CO—C_6H_5$ or $C_6H_5—\underset{\diagdown\,O\,\diagup}{CH—CH}—CO—C_6H_5$.

Dibenzoyl methane. Phenylbenzoyl ethylene oxide.

Since in our previous experiments on the action of sodium methylate upon benzylidene acetophenone dibromide only one compound was obtained, it seemed desirable to continue this investigation and to compare this compound with those described by Wislicenus.

The results of this investigation indicate that sodium methylate reacts in a manner somewhat different from that of alcoholic potash; and that the substance formed in this reaction, which was called dibenzoyl methane in the previous paper and was proved to be identical with the compound described under this name by Claisen, should be termed α-oxybenzylidene acetophenone.

EXPERIMENTAL.

Benzylidene Acetophenone, $C_6H_5—CH=CH—CO—C_6H_5$.—This compound is most conveniently prepared according to the method of Claisen[1] by the action of a small quantity of a 20 per cent. solution of sodium methylate upon a mixture of the molecular proportions of acetophenone and benzaldehyde. Claisen purified this product by repeated crystallizations from petroleum ether; this method is slow and rather unsatisfactory, since the compound is not easily soluble in this solvent, and it requires a number of recrystallizations to remove oily impurities. It was found that it could be purified readily and quickly by crystallizing from alcohol; it separates in large crystals, melting at 57° to 58°.

α- and β-Benzylidene Acetophenone Dibromides, $C_{15}H_{12}O.Br_2$.—By the addition of one molecular proportion of bromine to a solution of benzylidene acetophenone in chloroform, Claisen[2] obtained a dibromide, melting at 156° to 157°, which is difficultly soluble in cold alcohol. J. Wislicenus[3] also mentions that benzylidene acetophenone is almost completely precipitated from its chloroform solution, on the addition of one molecule of bromine, as a very difficultly soluble dibromide,

$$C_6H_5—CHBr—CHBr—CO—C_6H_5;$$

[1] Claisen and Claparède: *Ber. d. chem. Ges.*, **14**, 2463.
[2] Claisen: *Ber. d. chem. Ges.*, **14**, 2463.
[3] J. Wislicenus: *Ann. Chem.* (Liebig), **308**, 223.

after one crystallization from boiling alcohol, it is obtained in snow-white, pure crystals, melting at 156.5° to 157.5°. Hitherto, no mention appears to have been made of an isomeric dibromide and it is quite probable that it has been overlooked, although it is formed in small quantity whenever benzylidene acetophenone unites with bromine.

If a solution of 25 grams of benzylidene acetophenone in 125 cc. of ether be treated gradually with 20.8 grams (2 atoms) of bromine, and, after standing for a few minutes, the almost colorless solution is filtered by means of the pump from the thick, white precipitate, a considerable quantity of the new isomeric dibromide is obtained from the filtrate. The difficultly soluble compound is washed well with ether, crystallized from alcohol, and obtained as the pure white dibromide, melting at 157.5°. The analysis gave :

I. 0.1632 gram gave 0.1660 gram silver bromide.
II. 0.1510 gram gave 0.1530 gram silver bromide.

	Calculated for $C_{15}H_{12}O.Br_2$.	Found. I.	II.
Bromine.....	43.48	43.29	43.12

It is sparingly soluble in alcohol and ether, and will be termed α-benzylidene acetophenone dibromide in order to distinguish it from the lower melting, more soluble isomeric or β-dibromide.

The ethereal solution and wash-ether are treated with a small quantity of sulphurous acid in order to remove any slight excess of bromine, then washed well with water, and the ether allowed to evaporate ; the new β-dibromide is obtained from the residue. The latter is extracted with a limited quantity of boiling alcohol in order to separate a very small quantity of the comparatively insoluble α-compound, and, after evaporation of the alcohol, the β-dibromide is repeatedly crystallized from boiling alcohol. It separates in aggregates of small, fine needles, which melt at 108° to 109°. We usually obtained 3 to 4 grams of the β-dibromide by this method. It was analyzed with the following results :

I. 0.2002 gram gave 0.3570 gram carbon dioxide and 0.0635 gram water.
II. 0.3400 gram gave 0.3471 gram silver bromide.
III. 0.3436 gram gave 0.3509 gram silver bromide.

	Calculated for $C_{15}H_{12}O.Br_2$.	Found. I.	II.	III.
Carbon.....	48.91	48.63	....	....
Hydrogen	3.26	3.47	....	....
Bromine.....	43.48	....	43.44	43.45

It dissolves at 30° in 106 parts of ethyl alcohol, 96.7° Tr., while the α-dibromide, at the same temperature, requires 610 parts of alcohol. It is also more readily soluble in ether than the α-compound. On raising the temperature about 20° above its melting-point and then allowing to solidify, it again melts at 108.5°.

The crystalline forms of the two dibromides are quite distinct, the α- separating in short prisms, while the β-derivative crystallizes in fine needles.

It has also been observed that on brominating smaller quantities (about 5 grams) of benzylidene acetophenone at a time, and by adding the bromine rapidly, without cooling, a larger yield of the β-compound results. Although we usually employed ether as the solvent for the benzylidene acetophenone, nevertheless the formation of the isomeric bromide takes place when chloroform, carbon tetrachloride, or carbon disulphide is used. In all cases, however, the sparingly soluble α-dibromide (m. p. 157.5°) constitutes the chief product.

When the α-dibromide is heated under pressure with ethyl or methyl alcohol, hydrobromic acid is eliminated, but as yet no definite crystalline derivatives have been obtained which correspond with those so readily formed by merely boiling anisylidene acetophenone dibromide with ethyl or methyl alcohol.[1] On heating 20 grams of the α-dibromide with 100 cc. of methyl alcohol for three hours at 120°, a substance resulted which melted at 117° to 119°; this product has not, however, proved to be a definite chemical compound, and will be further studied. The change appears to take place between 110° and 125°; on heating the α-dibromide with methyl alcohol at a temperature below 110°, the unchanged compound is recovered; above 125° the substance suffers decomposition.

The Action of Two Molecules of Sodium Methylate upon the α-Dibromide.—To a solution of sodium methylate (8 grams of sodium in 200 cc. of methyl alcohol), 50 grams of α-benzylidene acetophenone dibromide were added, and boiled for thirty minutes in a reflux apparatus. Three hundred and fifty cc. of water were then introduced and the liquid rendered neutral or very slightly acid with dilute acetic acid. The oil which separated was extracted with ether, washed well with water, and dried over

[1] Pond and Shoffstall: This Journal, **22**, 668 and 670.

anhydrous sodium sulphate. After evaporation of the ether, some of the oil was distilled under diminished pressure ; it boiled at 206° to 210° under 12 mm. pressure, yielding a mobile, yellow oil, which had a slight odor of decomposition ; it did not become solid after standing in a closed vessel for several months. Analysis of this distillate gave the following results :

I. 0.2243 gram gave 0.6360 gram carbon dioxide and 0.1345 gram water.
II. 0.1978 gram gave 0.5609 gram carbon dioxide and 0.1226 gram water.

Analysis of oil prepared as above described, but which was not distilled, gave :

III. 0.1761 gram gave 0.5059 gram carbon dioxide and 0.0975 gram water.
IV. 0.1448 gram gave 0.4173 gram carbon dioxide and 0.0792 gram water.

	Calculated for $C_{16}H_{14}O_2$.	Found. I.	II.	III.	IV.
Carbon	80.64	77.33	77.34	78.36	78.63
Hydrogen	5.88	6.66	6.93	6.15	6.07

It was thought that the action of the sodium methylate consisted in removing one molecule of hydrogen bromide from the α-dibromide and replacing the remaining bromine atom with the methoxyl group, thus giving rise to the unsaturated *methyl ether of α-oxybenzylidene acetophenone*,

$$C_6H_5—C(OCH_3)=CH—CO—C_6H_5.$$

It has been impossible, however, to obtain analyses of this oil which would agree more closely with the calculated values for the methyl ether, although many analyses have been made on various samples of the oil purified by different methods. It is clear, therefore, that the oil is not a pure ether, but in the light of subsequent experiments it seems rather probable that the oil consists of a mixture of the ether with some compound, possibly derived from it. The oil reacts as an unsaturated compound ; its alcoholic solution at once decolorizes a permanganate solution; when dissolved in ether it absorbs bromine, but on evaporation of the solution hydrobromic acid is eliminated and a non-characteristic oil is obtained.

If the oil is the methyl ether suspected, or consists to some extent of this compound, it would be expected that dilute acids would convert it by hydrolysis into α-oxybenzylidene acetophenone. The following experiment indicates that this reaction actually does take place.

Some of the oil was placed into a flask and treated with fairly

concentrated hydrochloric acid ; in a very short time (one or two minutes) the entire quantity of oil was converted into the solid α-oxy-compound (m. p. 77° to 78°). This was repeated with different mineral acids of varying strength, also with acetic acid, and it was found that the oil was in each case converted into the solid compound, although with very dilute acids the action requires a longer time for its completion. On standing in an open dish in the laboratory the change is more gradual, but in a month's time the oil is almost completely converted into the solid α-oxy-compound. If this oil be placed in a closed vessel, it may be kept unchanged for a long time. We have retained a specimen in a desiccator, over fused calcium chloride, for nine months without the least trace of a solid being formed ; when, however, a drop of it was brought in contact with dilute acid, it was almost immediately changed into the solid compound.

When α-benzylidene acetophenone dibromide was treated with 2 molecules of sodium *ethylate* in the same manner as with the methylate, a reddish colored oil resulted ; this oil was analyzed with results similar to those above mentioned. It has properties similar to those of the oil resulting by the methylate treatment, decomposes on distillation at atmospheric pressure, distils with slight decomposition under reduced pressure, and is converted into α-oxybenzylidene acetophenone by contact with acids. It may contain the unsaturated *ethyl ether of α-oxybenzylidene acetophenone*, as indicated by the following experiment.

Eight grams of the red oil, previously well washed with water, dried over calcium chloride, and maintained for some time at 110°, were treated with 32 cc. of hydrochloric acid (1 : 1) ; in a short time the oil was converted into a solid, with a slight evolution of heat. The solid was filtered off, crystallized from alcohol and recognized as α-oxybenzylidene acetophenone, melting at 77° ; the presence of ethyl alcohol in the filtrate was readily and distinctly determined by means of the iodoform reaction. This change is doubtless to be represented by the formula

$$C_6H_5—C(OC_2H_5)=CH—CO—C_6H_5 + H—O—H = C_2H_5OH + C_6H_5—C(OH)=CH—CO—C_6H_5.$$

That is, the oil undoubtedly contains the ethyl ether which is hydrolyzed by dilute acids, yielding ethyl alcohol and the α-oxy-compound.

α-Oxybenzylidene Acetophenone, $C_6H_5—C(OH)=CH—CO—C_6H_5$.—This compound is readily obtained in good yield by treating the oil which results from the action of 2 molecules of sodium alcoholate upon α-benzylidene acetophenone dibromide with fairly concentrated hydrochloric acid. It is also easily formed by boiling the oil with acetic acid and then precipitating with ice-water. The crude product melts at 76° to 77°, and frequently has a slight yellow to reddish tinge. It is best purified by conversion into its copper salt and decomposition of the latter by dilute hydrochloric acid. It crystallizes well from methyl or ethyl alcohol; when the alcoholic solution is fairly concentrated, the crystals are obtained in the form of long needles, but from dilute solutions it separates in large plates or tablets; the latter form of crystals are also obtained from ether. Both modifications melt sharply at 77° to 78°, thus confirming J. Wislicenus'[1] observations regarding the melting-point of the so-called dibenzoyl methane. Analysis gave the results:

I. 0.2895 gram gave 0.8530 gram carbon dioxide and 0.1380 gram water.
II. 0.2997 gram gave 0.8880 gram carbon dioxide and 0.1500 gram water.

	Calculated for $C_{15}H_{12}O_2$.	Found. I.	II.
Carbon.....	80.36	80.35	80.80
Hydrogen.....	5.35	5.29	5.56

It may be noted here that this compound agrees completely in properties with the substance described by J. Wislicenus as α-oxybenzylidene acetophenone (formerly called dibenzoyl methane), but in no case have we obtained a trace of the isomeric compound observed by Wislicenus. It reacts readily with an alcoholic solution of copper acetate, forming the *copper salt*,[2] $C_{30}H_{22}O_4Cu$; this is insoluble in alcohol and ether, and only sparingly soluble in chloroform and benzene. It melts at 294° to 301° with decomposition.

The *iron salt* is precipitated on the addition of molecular quantities of ferric chloride and sodium acetate to an alcoholic solution of the α-oxy-compound; it is obtained in the form of a brick-red powder.

When a solution of α-oxybenzylidene acetophenone is boiled with 2 molecular proportions of hydroxylamine hydrochloride,

[1] J. Wislicenus: *Ann. Chem.* (Liebig), **308**, 228.
[2] J. Wislicenus: *Ibid.*, **308**, 231.

$\alpha\gamma$-diphenyl isoxazole,[1] $C_{15}H_{11}NO$, is formed ; it separates from alcohol in brilliant, white leaflets, and melts at 141° to 142°. The same compound results on treating the alcoholic solution of α-benzylidene acetophenone dibromide with aqueous solutions of hydroxylamine hydrochloride and potassium hydroxide ; it crystallizes from alcohol and melts at 141.5°.

On the addition of one molecule of bromine to a solution of the α-oxy-compound in chloroform, hydrogen bromide is given off and *mono*-bromdibenzoyl methane,[2] $C_{15}H_{11}BrO_2$, is produced. It separates from alcohol in fine, white crystals, melting at 91.5° to 92.5°.

On boiling β-benzylidene acetophenone dibromide with sodium alcoholate it was thought that a compound isomeric with α-oxybenzylidene acetophenone, and possibly identical with Wislicenus' second compound, might result ; this does not, however, appear to be the case. Ten grams of the β-dibromide were treated as usual with 2 molecules of sodium methylate ; after adding water and carefully neutralizing with dilute acetic acid, the resultant oil was extracted with ether, dried with anhydrous sodium sulphate, and the ether evaporated. The oil was then boiled for a short time with acetic acid and poured into ice-water; it solidified rapidly and crystallized from alcohol in long needles, melting at 77° to 78°; it separated from ether in plates of the same melting-point. In alcoholic solution it gave an immediate deep purple coloration with ferric chloride, and was quantitatively converted into the green copper salt by the addition of an alcoholic solution of copper acetate. It is therefore identical with the above described α-oxybenzylidene acetophenone.

In the future we propose to investigate more thoroughly the new β-dibromide, and to ascertain whether it is possible to convert this compound into an isomeric modification of benzylidene acetophenone.

[1] J. Wislicenus : *Ann. Chem.* (Liebig), **308**, 248 ; see also Goldschmidt : *Ber. d. chem. Ges.*, **28**, 2540.

[2] Neufville and Pechmann : *Ber. d. chem. Ges.*, **23**, 3377 ; J. Wislicenus : *Ann. Chem.* (Liebig), **308**, 247.

ON POSITIVE AND NEGATIVE HALOGEN IONS.

By Julius Stieglitz.

Received August 9, 1901.

At the end of an article on "The Reaction between Chlorine and Ammonia," published by W. A. Noyes and A. C. Lyons in a recent number of this Journal,[1] the interesting suggestion is made, that the chlorine may dissociate, before action, into positive as well as negative ions; the suggestion is accompanied by an invitation for discussion and further consideration.

The writer is induced to open the discussion because for a number of years the hypothesis of the existence of positive as well as negative ions of the three halogens, chlorine, bromine, and iodine, and notably of the formation of positive halogen ions by hypochlorous, hypobromous, and hypoiodous acids, with its consequences, has been publicly presented before the student and the professional body at the University of Chicago. The theory was supported, among other things, by the behavior of the above hypo-acids towards acids and by the strongly marked basic properties of the iodoso[2] and iodonium bases.[3]

As far as the former is concerned, the reaction

$$HOCl + HCl \rightarrowtail Cl_2 + H_2O$$

was considered as a purely ionic reaction,

$$\overset{-}{HO} + \overset{+}{Cl} + HOCl + \overset{+}{H} + \overset{-}{Cl} \rightarrowtail Cl_2 + H_2O, \text{ etc.};$$

hypochlorous acid ionizes very little but, like so many nearly neutral hydroxides, it ionizes both as a weak acid,

$$HOCl \rightleftarrows \overset{+}{H} + \overset{-}{ClO},$$

and at the same time as a still weaker base,

$$HOCl \rightleftarrows \overset{-}{HO} + \overset{+}{Cl},$$

much like aluminum hydroxide, the relative size of whose ionization constants is reversed. In the same way the action of chlorine on alkalies in aqueous solution was considered as a purely ionic reaction:

$$\overset{+}{Cl} + \overset{-}{Cl} + Cl_2 + \overset{+}{K} + \overset{-}{OH} \rightarrowtail \overset{+}{K} + \overset{-}{Cl} + HOCl, \text{ etc.}$$

[1] This Journal, **23**, 463.

[2] Willgerodt: *Ber. d. chem. Ges.*, **25**, 3494, etc.; V. Meyer: *Ibid.*, **25**, 2632, etc.

[3] Hartmann and V. Meyer: *Ibid.*, **27**, 426, etc.

The chief object of these lines is, however, to point out that the existence of *positive chlorine ions*, in aqueous solutions both of chlorine and of hypochlorous acid, can no longer be considered as a mere hypothesis, but must be accepted as proved experimentally by the splendid, quantitative experiments of Jakowkin[1] on the action of water on chlorine, although this consequence of his work has not heretofore been recognized.

Jakowkin's experiments prove conclusively that the reaction

$$HOCl + HCl \rightleftarrows H_2O + Cl_2$$[1]

is reversible; and also that it is an *ionic* reaction. A condition of equilibrium is produced according to

$$HOCl + \overset{+}{H} + \overset{-}{Cl} \rightleftarrows H_2O + Cl_2,$$[2]

and is dependent consequently on the concentrations of the hydrogen and chlorine ions as well as of the hypochlorous acid and chlorine. It is obvious, however, that if the reaction as far as the hydrochloric acid is concerned is an ionic one (which is rigidly proved) and also as far as the water is concerned (which is universally recognized), it must of necessity be an ionic reaction also for the *hypochlorous acid* (which must therefore dissociate, at least to a very slight extent, into hydroxyl and *positive chlorine ions*), and also be an ionic reaction for *chlorine*, which must dissociate partially into *positive* and negative ions. The very cause of hydrolysis as in all such cases and of the reversibility lies, not more in the minimal, but actual, ionization of water, than in the formation of these ions of hypochlorous acid and of chlorine, if the theory of ionization means anything at all.

It is curious that neither Jakowkin, nor any of the chemists who have commented on his work, seem to have drawn this obvious conclusion from it,—in the author's opinion the most important truth growing out of his fine experiments. Jakowkin assumes in his calculations that the hypochlorous acid is not dissociated into ions. Its dissociation constant undoubtedly is so small that, as in the case of water, it may well be neglected in these calculations; but, as in the well established ionization of water, no matter how small the ionization constant for hypochlo-

[1] *Zischr. phys. Chem.*, **29**, 613.

[2] Substances occurring in minimal quantities, *e. g.*, the ions of water, chlorine and hypochlorous acid, are, for the sake of simplicity, not represented in the equation.

rous acid (for $\overline{HO} + \dot{Cl}$) may be, it involves the *fact* of the existence of *positive chlorine ions*.

It must be added that these views would have been published long ere this, if it had not been the hope of the author to report at the same time on other direct experimental confirmations of them. Circumstances have made it impossible to undertake before this the delicate work involved; but in the ensuing year it is intended at least to study the behavior, of solutions of chlorine, hypochlorous acid, iodine chloride, etc., towards the electric current, in the hope of proving that, under suitable conditions, the migration of positive halogen ions to the negative pole will take place. Such a migration would decide the question, it seems to me, in the most direct and unquestionable fashion. I regret that the interesting paper of Professor Noyes and Mr. Lyons has made it necessary to publish these lines rather prematurely; but their invitation for discussion encourages me to do so before the completion of my own experiments.

UNIVERSITY OF CHICAGO,
August 3, 1901.

THE PHOTOMETRIC DETERMINATION OF SULPHATES.

BY D. D. JACKSON.

Received September 3, 1901.

THE time element enters largely into most transactions in the industrial world and chemistry as a pure science is not always to be considered. Exact methods, if time-consuming, must give place, in many cases, to rapid tests that give practical knowledge in the shortest possible limit of time.

If a trainload of coal is detained for inspection it is not feasible to wait a day or two for an ultimate analysis by organic combustion. The heating power is obtained in an hour and a half by calorimetry. By this same process, using the Mahler bomb, the determination of volatile sulphur, which would take two hours by ordinary chemical methods, may be accomplished by photometry in five minutes,—not with great accuracy, but with sufficient accuracy for practical purposes.

The physician in analyzing urine does not desire to know the exact percentage of sulphates present, but merely to what extent the amount present is below or above the normal. Photometry tells him this in a few minutes.

The determination of sulphates as an adulterant in cement where large constructional works are being carried out may necessitate the analysis of some twenty-five samples of cement daily. This is impractical, if not impossible, by ordinary methods; but by photometry it may be easily accomplished. A limiting figure is placed upon the amount of sulphates present in the cement by the specifications of the contract and, unless the figure found is very close to that of the specifications, the photometric process is quite accurate enough. Nearly all of the determinations may be disposed of in this manner, while the questionable ones may be determined, if necessary, by more accurate gravimetric methods. In this way a needless expense of time and energy is avoided. Many other instances might be cited where the photometric determination of sulphates would be highly practical.

Professor Hinds[1] was the first to suggest the photometric analysis of precipitates, and a year ago[2] he published tables to facilitate this process. Since that time the author has had occasion to use this method quite extensively in the determination of sulphur and sulphuric acid, and has made at the same time a large number of gravimetric determinations to check the results. Experiments have also been made with known solutions of sulphates and with sulphuric acid. It has been found in this manner that certain modifications of Professor Hinds' method greatly increase the ease and accuracy with which these determinations may be made.

It was noted that differences in the brightness of the candle employed and differences in the distance of the candle from the bottom of the tube, as well as of the eye of the observer from the top of the tube, made appreciable differences in the results. Accordingly, a series of experiments was made to determine the process whereby the most accurate figures might be obtained. The readings in many cases were made by four different observers, so that the personal element would be eliminated. Experiments were also made with the diaphenometer of Hornung,[3] modified by Parmelee and Ellms;[4] but, while this works very well in the determination of the turbidity in water, it was not found to be as convenient or as accurate for the determination of sulphates as the

[1] This Journal, **18**, 661.
[2] *Ibid.*, **22**, 269.
[3] *Eng. News*, April 2, 1896.
[4] *Tech. Quart.*, **12**, No. 2, June, 1899.

photometer of Hinds. The details of the method finally decided upon are as follows:

A very simple piece of apparatus is employed. It consists of a 100 cc. Nessler jar, 2.5 cm. in diameter, and 17 cm. to the 100 cc. mark. The dimensions need not be exact, but this is the size which is found to be most convenient. This jar is graduated from the bottom up in centimeters and millimeters to avoid constantly measuring the depth with a rule.

A standard candle is used, having just one candle power. Above this is suspended an iron ring with an indicator so that the top of the ring is always just three inches above the top of the candle itself. This brings the top of the flame in close proximity to the bottom of the tube, but just far away enough to prevent smoking or excessive heating.

The observations are made in a dark room and the candle is placed over a dark surface. The tube which is to contain the solution is enveloped in a brass holder which comes up almost to the 100 cc. mark and has a broad disk at the bottom which shields the eye from the strong light below. The bottom of this cylindrical shaped tube is entirely open except for a very narrow rim which serves to keep the glass tube in place. The inside of the holder is painted a dull black to prevent reflection.

The solution to be determined for sulphates is washed into the 100 cc. Nessler jar and made slightly acid with hydrochloric acid. Distilled water at room temperature is then added nearly to the 100 cc. mark. About 2 grams of pure solid barium chloride are added, and the solution made up exactly to the 100 cc. mark. A pure rubber stopper is placed in the top of the tube and the whole shaken thoroughly until the barium chloride is dissolved.

In a few minutes the solution is ready to be examined. The tube is placed in the brass holder and its contents are poured back and forth from the glass tube into a lipped beaker, keeping the precipitate constantly shaken up, so that throughout the liquid the turbidity is uniform.

When the holder containing the tube is placed on an iron ring suspended three inches above the top of the candle and the eye is held quite near the top of the glass tube, a point is finally reached where the flame of the candle just disappears. The height to which the solution stands in the tube (reading the bottom of the

meniscus) is then taken and from this reading the per cent. of sulphates may be calculated from the formula

$$x = \frac{0.0574}{y + 0.1},$$

where x equals grams of sulphur trioxide required, and y equals the depth in centimeters of the liquid in the cylinder.

This calculation is avoided and thereby considerable time saved by the use of the following table:

TABLE FOR THE PHOTOMETRIC DETERMINATION OF SULPHURIC ACID.

cm.	SO_3. Gram.	cm.	SO_3. Gram.	cm.	SO_3. Gram.	cm.	SO_3. Gram.
1.0	0.0522	4.0	0.0140	7.0	0.0081	10.0	0.0057
1.1	0.0478	4.1	0.0137	7.1	0.0080	10.2	0.0056
1.2	0.0442	4.2	0.0133	7.2	0.0079	10.4	0.0055
1.3	0.0410	4.3	0.0131	7.3	0.0078	10.6	0.0054
1.4	0.0383	4.4	0.0128	7.4	0.0077	10.8	0.0053
1.5	0.0359	4.5	0.0125	7.5	0.0076	11.0	0.0052
1.6	0.0338	4.6	0.0122	7.6	0.0075	11.2	0.0051
1.7	0.0319	4.7	0.0119	7.7	0.0074	11.4	0.0050
1.8	0.0302	4.8	0.0117	7.8	0.0073	11.6	0.0049
1.9	0.0287	4.9	0.0115	7.9	0.0072	11.8	0.0048
2.0	0.0273	5.0	0.0113	8.0	0.0071	12.0	0.0047
2.1	0.0261	5.1	0.0110	8.1	0.0070	12.2	0.0047
2.2	0.0250	5.2	0.0108	8.2	0.0069	12.4	0.0046
2.3	0.0239	5.3	0.0106	8.3	0.0068	12.6	0.0045
2.4	0.0230	5.4	0.0104	8.4	0.0068	12.8	0.0044
2.5	0.0221	5.5	0.0103	8.5	0.0067	13.0	0.0044
2.6	0.0213	5.6	0.0101	8.6	0.0066	13.5	0.0042
2.7	0.0205	5.7	0.0099	8.7	0.0065	14.0	0.0041
2.8	0.0198	5.8	0.0097	8.8	0.0064	14.5	0.0039
2.9	0.0191	5.9	0.0096	8.9	0.0064	15.0	0.0038
3.0	0.0185	6.0	0.0094	9.0	0.0063	15.5	0.0037
3.1	0.0179	6.1	0.0093	9.1	0.0062	16.0	0.0036
3.2	0.0173	6.2	0.0091	9.2	0.0062	16.5	0.0035
3.3	0.0168	6.3	0.0090	9.3	0.0061	17.0	0.0034
3.4	0.0164	6.4	0.0088	9.4	0.0060	17.5	0.0033
3.5	0.0159	6.5	0.0087	9.5	0.0060	18.0	0.0032
3.6	0.0155	6.6	0.0086	9.6	0.0059	18.5	0.0031
3.7	0.0151	6.7	0.0084	9.7	0.0059	19.0	0.0030
3.8	0.0147	6.8	0.0083	9.8	0.0058	19.5	0.0029
3.9	0.0144	6.9	0.0082	9.9	0.0057	20.0	0.0029

SULPHATE IN CEMENT.

Treat 1 gram of cement with strong hydrochloric acid, add water and evaporate to dryness. Add a small amount of concen-

trated hydrochloric acid, then add an equal amount of boiling water and filter into a 100 cc. graduated tube, make up to the mark with cold water, and proceed with the photometric method as directed.

If exactly 1 gram is taken, and the reading on the tube is 4.3 cm., then from the table, 1 gram contains 0.0131 gram of sulphur trioxide, or 1.3 per cent. sulphur trioxide.

Specifications usually state that not over 1.5 per cent. sulphur trioxide can be accepted. 2 per cent. is sometimes used as a limiting figure.

SULPHATE IN URINE.

Filter the urine, if turbid, and take 10 cc., make it slightly acid with hydrochloric acid and add water nearly to the 100 cc. mark. Add about 2 grams of solid barium chloride, make up to the 100 cc. mark, and proceed as directed in the method.

If 10 cc. are taken and the reading on the tube is 4.6, then from the table, 10 cc. equals 0.0122 gram sulphur trioxide, or 0.12 per cent.

Normal urine varies from 0.10 to 0.15 per cent. sulphur trioxide.

SULPHATE IN WATER.

100 cc. may be taken for well waters, but some well waters and many surface waters will need to be concentrated in order to get accurate results.

A quick determination in waters low in sulphates may be roughly made by taking 100 cc. of water, acidifying slightly with hydrochloric acid and adding solid barium chloride. After shaking well, the turbidity is compared with silica standards sidewise toward the light. These silica standards have been used in the determination of the turbidity of drinking water.[1]

A standard of ten in silica is equivalent to a turbidity produced by 1.45 parts per million of sulphur trioxide. The photometric method, while not as rapid as this for solutions requiring concentration, is, however, much more accurate. The reason for this will be shown by a study of the diagram given later, in which it is seen that the results do not follow the reciprocal curve.

SULPHATE IN COAL.

After fusion by the ordinary method, the sulphate in coal may

[1] Whipple, G. C., and Jackson, D.D.: *Tech. Quart.*, **12**, No. 4, Dec. 1899: **13**, No. 3, Sept., 1900.

be determined photometrically; but when the Mahler bomb is used, the volatile sulphur is all in solution in the water at the bottom of the bomb. This water is filtered and titrated with 0.1 normal sodium carbonate, using methyl orange as an indicator to get the nitric acid present. It is then ready for the determination of sulphur by photometry. The pink color of the solution does not interfere with the results.

The following is a special table calculated for the determination of sulphur:

TABLE FOR THE PHOTOMETRIC DETERMINATION OF SULPHUR.

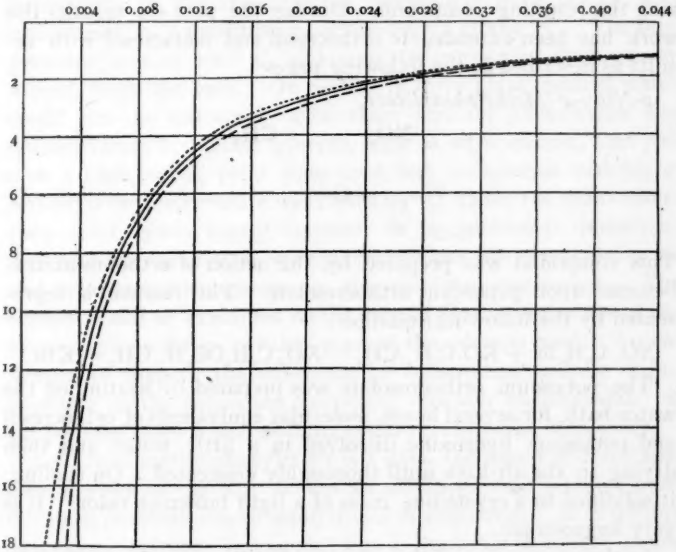
cm.	Sulphur. Gram.	cm.	Sulphur. Gram.	cm.	Sulphur. Gram.	cm.	Sulphur. Gram.
1.0	0.0209	4.0	0.0056	7.0	0.0032	10.0	0.0023
1.1	0.0191	4.1	0.0055	7.1	0.0032	10.2	0.0022
1.2	0.0177	4.2	0.0053	7.2	0.0032	10.4	0.0022
1.3	0.0164	4.3	0.0052	7.3	0.0031	10.6	0.0022
1.4	0.0153	4.4	0.0051	7.4	0.0031	10.8	0.0021
1.5	0.0144	4.5	0.0050	7.5	0.0030	11.0	0.0021
1.6	0.0135	4.6	0.0049	7.6	0.0030	11.2	0.0020
1.7	0.0128	4.7	0.0048	7.7	0.0030	11.4	0.0020
1.8	0.0121	4.8	0.0047	7.8	0.0029	11.6	0.0020
1.9	0.0115	4.9	0.0046	7.9	0.0029	11.8	0.0019
2.0	0.0109	5.0	0.0045	8.0	0.0028	12.0	0.0019
2.1	0.0104	5.1	0.0044	8.1	0.0028	12.2	0.0019
2.2	0.0100	5.2	0.0043	8.2	0.0028	12.4	0.0018
2.3	0.0096	5.3	0.0042	8.3	0.0027	12.6	0.0018
2.4	0.0092	5.4	0.0042	8.4	0.0027	12.8	0.0018
2.5	0.0088	5.5	0.0041	8.5	0.0027	13.0	0.0018
2.6	0.0085	5.6	0.0040	8.6	0.0026	13.5	0.0017
2.7	0.0082	5.7	0.0040	8.7	0.0026	14.0	0.0016
2.8	0.0079	5.8	0.0039	8.8	0.0026	14.5	0.0016
2.9	0.0076	5.9	0.0038	8.9	0.0026	15.0	0.0015
3.0	0.0074	6.0	0.0038	9.0	0.0025	15.5	0.0015
3.1	0.0072	6.1	0.0037	9.1	0.0025	16.0	0.0014
3.2	0.0069	6.2	0.0036	9.2	0.0025	16.5	0.0014
3.3	0.0067	6.3	0.0036	9.3	0.0024	17.0	0.0014
3.4	0.0066	6.4	0.0035	9.4	0.0024	17.5	0.0013
3.5	0.0064	6.5	0.0035	9.5	0.0024	18.0	0.0013
3.6	0.0062	6.6	0.0034	9.6	0.0024	18.5	0.0012
3.7	0.0060	6.7	0.0034	9.7	0.0024	19.0	0.0012
3.8	0.0059	6.8	0.0033	9.8	0.0023	19.5	0.0012
3.9	0.0058	6.9	0.0033	9.9	0.0023	20.0	0.0012

If 1 gram of coal is taken and the reading on the photometer is 3.1 cm., then from the table the amount present is 0.0072 gram, and the coal contains 0.7 per cent. of sulphur. A coal should

not contain over 1 per cent. of volatile sulphur; 1.5 per cent. may sometimes be taken as a limit.

In the accompanying diagram the long dash line is the curve produced by the precipitation of barium sulphate where the ordinates are centimeters in depth, and the abscissas are grams of sulphur trioxide when reading with the photometer. The unbroken line is the reciprocal curve and the dotted line is the curve produced by standard silica made from diatomaceous earth.

The silica curve shows the form of curve produced by an absolutely insoluble substance and its variation from the reciprocal curve shows the effect of the cutting out of light by the water itself.



The difference between the silica curve and the sulphate curve represents the solubility of the barium sulphate. This explains why the formula takes the form

$$x = \frac{0.0574}{y + 0.1},$$

when according to optics the denominator should be $(y - a)$ instead of $(y + a)$.

A wide field is open for experiments upon the photometric

determination of other precipitates and, in the future, there is no reason why photometry should not take as important a place in chemical analysis as that now occupied by colorimetry.

MT. PROSPECT LABORATORY,
BROOKLYN, N. Y.

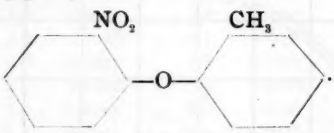
DERIVATIVES OF PHENYLETHER, II.

BY ALFRED N. COOK.

Received August 27, 1901.

IN a paper[1] published a few months since by A. N. Cook and H. W. Hillyer a number of derivatives of phenylether were described which had been prepared by acting on potassium paracresolate with orthobromnitrobenzene, and reducing and oxidizing the resulting compound. During the past six months the work has been extended to orthocresol and metacresol with results as described in the following pages :

2-Nitro-2'-Methylphenylether,



This compound was prepared by the action of orthobromnitrobenzene upon potassium orthocresolate. The reaction is represented by the following equation :

$$NO_2.C_6H_4Br + KO.C_6H_4.CH_3 = NO_2.C_6H_4OC_6H_4.CH_3 + KBr.$$

The potassium orthocresolate was prepared by heating on the water-bath, for several hours, molecular equivalents of orthocresol and potassium hydroxide dissolved in a little water, and then drying in the air-bath until thoroughly desiccated. On cooling, it solidified to a crystalline mass of a light brownish color. It is very hygroscopic.

In the preparation of the ether, molecular equivalents of potassium orthocresolate and orthobromnitrobenzene were heated in an oil-bath. At 137° C., a gentle ebullition began which increased for a few minutes, although the containing flask was removed from the bath, and then gradually subsided. The temperature also rose several degrees during the action. When the action had ceased there remained a copious precipitate of potassium bromide and a supernatant brownish-black liquid. When cool the liquid was

[1] *Am. Chem. J.*, **24**, 525-529.

extracted with ether. The ether extract was washed with a weak water solution of potassium hydroxide to remove any free cresol which might be preseht. The orthobromnitrobenzene which remained unacted upon was distilled off with steam and the phenylether was distilled under diminished pressure.[1] Fourteen grams of the crude ether were obtained from 26 grams of orthobromnitrobenzene, or 40 per cent. of theory. Twenty-six per cent. of the orthobromnitrobenzene remained unacted upon.

When two molecular equivalents of the orthobromnitrobenzene were employed to one of potassium orthocresolate, a temperature of 170° C. was required to induce reaction and the yield was much less than with equimolecular quantities. When molecular equivalents of the two reacting compounds were heated with orthocresol as a menstruum, action began at 165° C. The temperature rose to 200° C. although the containing flask was removed from the bath. On cooling, a tarry mass resulted which could not be extracted with ether and no phenylether was obtained from it. Other solvents, such as nitrobenzene, that possess a high boiling-point were used, but no reaction took place, although the temperature was raised 65° C. above the point where they react, when heated together in equimolecular quantities. The first instance would be explained by the free cresol acting on the orthobromnitrobenzene or the resulting compound. The second would be explained on the ground that no ionization of the two reacting substances takes place in the solvents used. An endeavor to prepare the substance by substituting sodium orthocresolate for the potassium compound was also unsuccessful. A tar resulted from which nothing could be extracted with ether.

2-Nitro-2′-methylphenylether is a dark red liquid of 1.195 specific gravity at 20° C. It has an oily taste, and a fruity odor which is probably due to small traces of impurities. It is soluble in organic solvents in general, but is insoluble in water ; is not volatile with steam ; and when subjected to a temperature of 18° C. for several hours it did not solidify. It decomposes when boiled under ordinary atmospheric pressure, but distils unchanged at 194°–196° C. under a pressure of 14 mm. 0.6925 gram of the liquid, dissolved in 41.8 grams of absolute alcohol, gave a rise of the boiling-point of 0.095°. This gives 200.6 as the molecular

[1] I am indebted to the kindness of Dr. H. W. Hillyer, of the University of Wisconsin, for distilling this compound for me under diminished pressure, as well as the 2-nitro-3′-methylphenylether mentioned farther on.

weight. Theory requires 229. Potassium dichromate in acetic acid solution does not oxidize the side-chain to carboxyl as in case of 2-nitro-4'-methylphenylether. The compound is burned completely when the temperature is but slightly raised. Analyses resulted as follows:

	Calculated for $C_{13}H_{11}NO_3$.	Found. I.	II.
Carbon	68.12	67.97	68.22
Hydrogen	4.83	....	4.50

2-Amino-2'-Methylphenylether Hydrochloride, $CH_3.C_6H_4OC_6H_4.NH_2.HCl$.—The amido compound was prepared by dissolving the previously described phenylether in alcohol and reducing with tin and hydrochloric acid while warming on the water-bath. The action was allowed to continue until a test portion yielded no precipitate when diluted with a large amount of water. The tin was precipitated with hydrogen sulphide and the solution concentrated on the water-bath, when it assumed a slightly pink tint. The hydrochloride does not crystallize but simply separates out in the form of a snow-white wax which coheres readily when pressed together with the fingers. It is readily soluble in ether and alcohol, and moderately soluble in water. A water solution does not yield a chlorplatinate with hydrochlorplatinic acid. Of several attempts to prepare the amido derivative only one was successful. It would invariably decompose while concentrating on the water-bath. The specimen obtained, however, was perfectly stable. It was kept for several days, a part of the time in contact with water. In attempting to prepare the free base by precipitating with ammonia, it decomposed before it could be filtered.

2-Nitro-2'-Methylphenylether Sulphonic Acid, $NO_2.C_{12}H_7O.CH_3.SO_3H$.—The free acid was prepared by dissolving 2-nitro-2'-methylphenylether in concentrated sulphuric acid, diluting with a large amount of water, precipitating the excess of sulphuric acid with lead nitrate, and removing the excess of lead with hydrogen sulphide. The solution was then evaporated on the water-bath and the acid desiccated over sulphuric acid.

It is a reddish-yellow, sirupy liquid which becomes somewhat viscous on cooling, and has an intensely bitter taste. It is readily soluble in petroleum ether, glacial acetic acid, wood alcohol, ethyl alcohol, benzene, nitrobenzene, dimethyl aniline, glycerine, aldehyde, and benzaldehyde. One part of the acid is soluble in

about 2.5 parts of water at 80° C. and considerably less soluble in cold water. A weak solution of the acid does not yield a precipitate with any of the metals. Its composition was determined by the analyses of some of its salts which are given below.

Barium Salt, $(NO_2.C_{12}H_7O.CH_3.SO_3)_2Ba$.—This salt was prepared by adding sufficient barium chloride to the diluted sulphuric acid solution of the ether to remove the excess of sulphuric acid and change all of the free sulphonic acid to the barium salt. Owing to the fact that the salt is only sparingly soluble in cold water, most of it was precipitated along with the barium sulphate and had to be extracted from it with boiling hot water, from which it crystallized on cooling in light, fluffy, radial aggregations of fine, cream-white needles. It is almost without taste. 7.45 parts of the salt are soluble in 1000 parts of boiling hot water and 1.2 parts are soluble in 1000 parts of water at 31° C. The water solution is almost colorless. This salt is the least soluble of any here described, and as a consequence the most easily purified. Two determinations of the barium after crystallizing the compound four times from hot water and drying at 150° C. resulted as follows:

I. 0.2394 gram of the substance yielded 0.0731 gram of barium sulphate.
II. 0.5112 gram of the substance yielded 0.1567 gram of barium sulphate.

	Calculated for $(C_{13}H_{10}O_6SN)_2Ba$.	Found. I.	Found. II.
Barium	18.18	17.96	18.04

Strontium Salt, $(CH_3.C_{12}H_7O.NO_2.SO_3)_2Sr + 2H_2O$.—The strontium salt was prepared by the same general method as the barium salt. Strontium nitrate was used to precipitate the excess of sulphuric acid. Some of the salt was thrown down with the strontium sulphate and was extracted with hot water. It crystallizes from a hot water solution in crystalline grains except when allowed to crystallize very slowly, when the crystals resemble snowflakes in form. They are brownish yellow in color and about 2 mm. in diameter. The water solution of the salt is yellow. Twenty parts of the compound are soluble in 1000 parts of boiling hot water, and 6.8 parts are soluble in 1000 parts of water at 31° C. On being dried in the air-bath at 110° C. it lost in weight corresponding to two molecules of water.

I. 0.2326 gram of the substance yielded 0.0104 gram of water and 0.0576 gram of strontium sulphate.

II. 0.2385 gram of the substance yielded 0.0108 gram of water and 0.0595 gram of strontium sulphate.

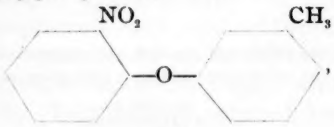
	Calculated for $(CH_3.C_{12}H_7O.NO_2.SO_3)_2Sr + 2H_2O$.	Found. I.	II.
Strontium	11.84	11.82	11.91
Water	4.87	4.47	4.53

Lead Salt, $(CH_3C_{12}H_7O.NO_2.SO_3)_2Pb$.—The same general method was used in the preparation of the lead salt as with the two preceding. Owing to the greater solubility, however, it was not necessary to digest the lead sulphate precipitate with hot water, but it was necessary to concentrate the solution in order to induce crystallization. Its water solution is a deep yellow. It crystallizes in well defined, yellow, crystalline grains. 81.7 parts of the salt are soluble in 1000 parts of boiling water, and 35 parts are soluble in 1000 parts of water at 31° C.

I. 0.3600 gram of the substance yielded 0.1001 gram of lead oxide.
II. 0.2816 gram of the substance yielded 0.0766 gram of lead oxide.

	Calculated for $(CH_3.C_{12}H_7O.NO_2.SO_3)_2Pb$.	Found. I.	II.
Lead	25.15	25.55	25.24

2-Nitro-3'-Methylphenylether,



was prepared by the same general method as the 2-nitro-2'-methylphenylether described in the preceding pages, from potassium metacresolate and orthobromnitrobenzene. The potassium orthocresolate was prepared in the same manner as the potassium orthocresolate. It is a light brown crystalline solid, when prepared by this method. It melts at about 55° C., and liquefies by absorption of water when allowed to remain in contact with the air.

When the temperature of the two reacting substances was raised to 100° C. a gentle ebullition began which increased and the temperature rose to 145° C., although the containing flask was removed from the oil-bath. The action continued for about five minutes and then subsided. There remained a copious precipitate of potassium bromide and a supernatant brown liquid. The yield was almost quantitative in the first experiment but not so good in the second.

This compound is a red, oily liquid. From its appearance it could not be distinguished from 2-nitro-2'-methylphenylether. Its specific gravity is 1.208 at 27° C. It is not volatile with steam; it has an oily taste and a slight, fruity odor, probably due to small quantities of impurities; decomposes when boiled under ordinary atmospheric pressure, but under 30 mm. pressure it distils without decomposition at 223° C. It is very soluble in alcohol, ether, benzene, chloroform, acetic acid, and other organic solvents. It is insoluble in water. An attempt to oxidize the side-chain to carboxyl was unsuccessful. It seemed to burn completely. Owing to the small amount of the substance at hand I was unable to make an analysis, but its composition is sufficiently shown by the analysis of the barium salt of the sulphonic acid derivative.

2-Amino-3'-Methylphenylether Hydrochloride, $CH_3.C_6H_4OC_6H_4.NH_2.HCl$, was prepared in the same manner as the corresponding hydrochloride of 2-amino-2'-methylphenylether. It was more stable, however, during the process of preparation, only decomposing slightly when evaporating the water solution on the water-bath. It is a clear, viscous substance, very soluble in alcohol and ether, but quite sparingly soluble in water. A water solution does not yield a precipitate with hydrochlorplatinic acid. An attempt to prepare the free base was unsuccessful. It was precipitated from its water solution with ammonia, but it decomposed under the bell-jar over sulphuric acid before it could be thoroughly dried.

2-Nitro-3'-Methylphenylether Sulphonic Acid, $NO_2.C_{12}H_7O.CH_3.SO_3H$, was prepared by the same method as the corresponding derivative of 2-nitro-2'-methylphenylether. On concentrating the water solution it crystallizes in short, well defined, yellowish brown needles. It possesses a slightly bitter taste, and is soluble in alcohol, ether, and other organic solvents. Its water solution is yellow and dyes the hands yellow.

The Barium Salt, $(NO_2.C_{12}H_7.CH_3.SO_3)_2Ba + 2H_2O$, was prepared in the same manner as the barium salt of 2-nitro-3'-methylphenylether sulphonic acid. It separates from a weak water solution in crystals about 2 mm. in diameter which resemble snowflakes in appearance, but with a heavier structure. They are light brown in color and are composed of little balls connected to

×9

the central portion by ligaments as shown in the accompanying drawing. Eleven parts of the salt are soluble in 1000 parts of water at 82° C. and 6.1 parts are soluble in 1000 parts of water at 35° C. When dried in the air-bath at 100° C. for an hour it lost in weight corresponding to two molecules of water.

I. 0.2583 gram of the substance yielded 0.0110 gram of water.

II. 0.2363 gram of the substance yielded 0.0098 gram of water and 0.0683 gram of barium sulphate.

	Calculated for $(CH_3.C_{12}H_7.NO_2.SO_3)_2Ba + 2H_2O$.	I.	Found. II.
Barium	17.36	....	17.01
Water	4.05	4.26	4.15

2-Nitro-4'-methylphenylether Sulphonic Acid, $NO_2.C_{12}H_7O.CH_3.SO_3H$, was made from the corresponding ether previously described[1] by the same method as the analogous compounds already described in this paper. The heat of the boiling water-bath was necessary to induce solution of the ether in the concentrated sulphuric acid. No charring was produced as stated in a previous article.[2] The substance then used, as was afterwards known, was not quite pure. On decomposing the lead salt with hydrogen sulphide and concentrating the water solution, the acid crystallizes out in well-defined crystals of a reddish brown color and a slightly bitter taste. After being desiccated over sulphuric acid it increases in weight rapidly on coming in contact with the air. Its water solution is very yellow. It is readily soluble in alcohol, ether, benzene, glacial acetic acid, and other organic solvents. Ninety-eight parts of the acid are soluble in 1000 parts of water at 31° C. Its water solution does not give a precipitate with any of the metals. Its composition was determined by analyzing the barium salt.

Barium Salt, $(NO_2.C_{12}H_7O.CH_3.SO_3)_2Ba + 5H_2O$.—The barium salt was prepared in the same manner as its analogues. Its solubility in water is the highest and the number of molecules of water of crystallization the greatest of any of the salts described. On account of its greater solubility it was the most difficult to purify by recrystallization. It crystallizes out in yellowish brown warts about $\frac{1}{4}$ inch in diameter on the average. It is insoluble in organic solvents in general, but is soluble in both methyl and

[1] *Am. Chem. J.*, **24**, 526.

[2] *Loc. cit.*, p. 527.

ethyl alcohol containing a very little water. 691 parts of the salt are soluble in 1000 parts of water at 80° C. and 147 parts are soluble in 1000 parts of water at 27° C. On being heated in the air-bath at 100°–110° C. it becomes somewhat lighter in color and loses in weight corresponding to five molecules of water of crystallization.

0.1792 gram of the substance yielded 0.0167 gram of water and 0.0499 gram of barium sulphate.

	Calculated for $(NO_2.C_{12}H_7O.CH_2.SO_3)_2Ba+5H_2O$.	Found.
Barium	16.25	16.35
Water	9.54	9.33

This study is being continued and extended to the reaction between parabromnitrobenzene and the cresols.

MORNINGSIDE COLLEGE,
SIOUX CITY, IOWA,
August 10, 1901.

OPTICAL ROTATIONS OF CERTAIN TARTRATES IN GLYCEROL.

BY J. H. LONG.

Received August 17, 1901.

NEARLY all active substances exhibit different rotations in different solvents. In some cases the causes of these variations, are known while in other and numerous instances no satisfactory explanation of the variable activity has yet been given. The several important factors in this variation in specific rotation have been grouped by Landolt as follows:

a. Electrolytic dissociation in aqueous solution.
b. Formation or breaking down of molecular aggregations.
c. Presence of complex so-called crystal molecules in solution.
d. Formation of hydrates or corresponding bodies with solvent.
e. Hydrolysis.

It was pointed out by Landolt, and confirmed by Oudemans, that in dilute solutions the molecular rotations of salts of active acids are independent of the base combined with the acid, and that in salts of active bases the molecular rotations are independent of the inactive acid. This is well illustrated by the following table in which $[M]_D$ refers to the molecular rotation.

	$[M]_D$.
$(NH_4)_2C_4H_4O_6$	63.0
$Na_2C_4H_4O_6$	59.9
$K_2C_4H_4O_6$	64.4
$NaNH_4C_4H_4O_6$	61.7
$KNH_4C_4H_4O_6$	63.8
$KNaC_4H_4O_6$	62.4
$MgC_4H_4O_6$	61.7

For a number of solutions containing thallium tartrate and thallium double tartrates, I found molecular rotations much smaller than these for the higher concentrations but approaching them on increasing dilution.[1]

Hädrich, in 1893,[2] gave the most plausible explanation of this behavior when he showed by conductivity experiments that the variations in molecular rotation keep pace with variations in the degree of ionization. He pointed out that for many cases of dissolved active salts the molecular rotation in dilute solution is independent of the inactive ion.

From this standpoint it is of interest to note the behavior of bodies in glycerol in which solvent the degree of ionization must be relatively small. The compounds which I have examined to test this were the following: potassium sodium tartrate, potassium antimonyl tartrate, potassium boryltartrate, ammonium tartrate, ammonium hydrogen tartrate, and ammonium antimonyl tartrate. These salts were all prepared in condition of high purity and were dissolved in a special glycerol kindly prepared for me by Dr. A. G. Manns, chief chemist of Armour & Co., to whom my thanks are due. This glycerol was not only practically anhydrous but was remarkably free from traces of other bodies.

It is difficult to secure clear crystals of the ammonium antimonyl tartrate, as on concentration of the solution a gummy mass is usually obtained. But after many trials one solution deposited an abundant crop of crystals, which by determination of the antimony and the water were found to have the composition $(NH_4)(SbO)C_4H_4O_6 + \frac{1}{2}H_2O$. Another product secured had approximately the composition $(NH_4)(SbO)C_4H_4O_6 + 2\frac{1}{2}H_2O$.

The tartrates of ammonium and the potassium boryltartrate were made in the laboratory by well-known methods. The following table contains the results of polarizations made partly with

[1] *Am. J. Sci. and Arts*, **38**, 264.
[2] *Ztschr. phys. Chem.*, **12**, 476.

the large Landolt-Lippich instrument in a 400 mm. tube, and partly in a Laurent instrument from Schmidt and Haensch with a 200 mm. tube.

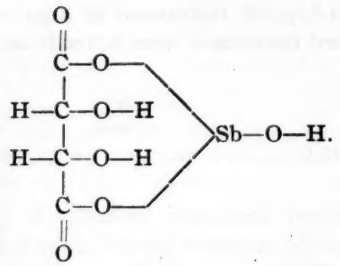
Salt.	$[\alpha]_D^{20}$ for water.	$[\alpha]_D^{20}$ for glycerol.
$KNaC_4H_4O_6.4H_2O$	22.1° $c=5$ to 30	28.85° $c=5$
		28.35° $c=10$
		27.87° $c=15$
		27.40° $c=20$
		26.96° $c=25$
$KSbOC_4H_4O_6.\frac{1}{2}H_2O$	140.69° $c=2$	139.25° $c=2$
	141.27° $c=5$	141.17° $c=3$
	141.40° $c=6$	143.75° $c=4$
$KBOC_4H_4O_6$	58.10° $c=5$	30.9° $c=5$
$(NH_4)_2C_4H_4O_6$	34.50° $c=5$	43.50° $c=4$
$(NH_4)HC_4H_4O_6$	26.0° $c=1.5$	27.7° $c=0.75$
$(NH_4)SbOC_4H_4O_6.\frac{1}{2}H_2O$	150.0° $c=5$	146.10° $c=3$
		146.25° $c=4$
$NH_4SbOC_4H_4O_6.2\frac{1}{2}H_2O$	115.7° $c=5$	109.37° $c=4$

It will be observed in this table that the values of the specific rotations obtained in glycerol solution for potassium sodium tartrate, ammonium tartrate and ammonium hydrogen tartrate are greater than the rotations found in aqueous solution. In the first two cases the differences are extremely marked and the active ion is probably no longer the simple group, $C_4H_4O_6$. It is interesting to note in the case of Rochelle salt that the specific rotation is greatest in the glycerol solution of lowest concentration, or greatest degree of separation into single molecules.

The behavior of the two antimonyl tartrates is the most characteristic and important. We have here very high specific rotations in water, and but slightly different in glycerol. For the first of these substances Hädrich[1] has shown that there is almost no dissociation, and it is evident that the same ion is active in both aqueous and glycerol solutions. The molecular rotations of the two bodies in water are almost identical, but for the ammonium salt the molecular rotation in glycerol is a little lower. This concordant behavior naturally suggests the existence of a peculiar acid as active in these salts, and this may be, as Clarke's investigations[2] of some years ago seemed to prove, a body of the formula

[1] *Loc. cit.*

[2] *Am. Chem. J.*, **2**, 319.



The heavy ion of this acid has about seven times the effect on the polarized ray that is exerted by the lighter ion of the ordinary tartaric acid in both media.

But the case is different with the potassium boryltartrate, the composition of which has usually been assumed as similar to that of the antimony compound. We have here a much lower rotation in glycerol than in water, indicating the presence of different active ions in the two media. By hydrolysis in aqueous solution, as found by Hädrich,[1] the rotation decreases very rapidly and finally approaches that of the simpler ion, $C_4H_4O_6$. It is likely therefore that this body is not perfectly analogous to tartar emetic, as in their electrical and optical behavior the arsenyl tartrates are likewise not.

It is well-known that glycerol is a remarkably good solvent for boric acid, and the low rotation of the borotartrate in that medium may possibly be accounted for by assuming that in the solution the whole or a part of the boric acid radical is withdrawn to form a glycerol compound. This kind of hydrolysis would leave then a simple tartrate. The molecular rotation calculated from the glycerol solution is almost normal which lends color to the assumption, while that from the water solution is nearly twice as great.

The main points shown then with reference to the glycerol solutions are these: The simple metallic tartrates examined dissolve in glycerol and show a larger specific rotation than in water. The antimonyl tartrates, which are but slightly dissociated, show nearly the same rotation in water and glycerol, and their behavior in general suggests a composition different from that usually assumed. Potassium boryltartrate shows in glycerol a much lower

[1] *Loc. cit.*

rotation than in water, the calculated specific rotation suggesting the presence of the simple tartrate in the glycerol solution.

NORTHWESTERN UNIVERSITY, CHICAGO,
August 15, 1901.

NOTE ON THE DETERMINATION OF SILICON IN STEEL.

BY GEORGE AUCHY.

Received August 26, 1901.

ALTHOUGH it has been mentioned by Dudley that silicon results in steel by Drown's method are apt to be low, on account of the iron sulphate enclosing and protecting the silicic acid from the dehydrating action of the sulphuric acid, it is probable that this fact is one not generally appreciated by chemists.

When the method is used for pig iron, as was originally intended by its author, there is no error from this cause less;[1] but in steel the loss amounts to from 0.01 per cent. to 0.035 per cent. silicon in medium silicon (0.15 to 0.20 per cent.) steels, which is too much to be ignored. Dr. Dudley thinks that it may be prevented by taking great pains to insure sufficient contact by stirring. Four experiments made by the writer, in which five minutes' stirring in each case was done after the appearance of sulphuric fumes, showed this to be true, only 0.006 per cent. silicon in each case being lost. But in a busy laboratory with many silicon determinations being made, or with much other work demanding the attention of the operator, this stirring adds considerably to the labor of the method, and the time it requires can hardly be allowed. Says Dr. Dudley: "If by some modification the iron salts could be kept in solution until the silica is rendered quite insoluble, it would apparently be a decided step forward with this method."

Several years ago the writer found that if aqua regia be used in the method instead of nitric acid alone, and the proportion of strong sulphuric acid be about 3.2 cc. per gram of drillings,[2] the iron salt in that case did not separate out until just a little before

[1] There is loss, it is true, of about 0.10 to 0.15 per cent. silicon in high silicon pig, but it is due to the same cause (whatever this cause may be) that in silicate analyis brings the result too low. It is a well-known fact that from 1.5 to 3 per cent. of the total silica of silicates remains in the filtrate from the first silica separation, no matter what method of dehydration be employed, or how many evaporations be made before filtration (Cameron: *Chem. News*, **69**, 171). We should therefore expect the same proportion of loss in pig iron and steel analysis, or about 0.006 per cent. silicon in a 0.20 per cent. silicon steel, and about 0.10 per cent. in a 3 per cent. silicon pig iron.

[2] The liquid boiled down rapidly in a capacious covered casserole (evaporating dishes do not serve) on a very hot plate.

the appearance of sulphuric fumes, and it was thought therefore that this process favored the dehydration of the silicic acid. Later it was found, however, that with one evaporation the loss of silica was usually just as great or greater than in using the regular method.

Upon experimenting with the old Swedish method reintroduced by Dr. Kinsey, and which consists in the use of sulphuric acid alone,[1] without nitric or any other acid, it was found that the silica lost by incomplete dehydration in this method was usually less than 0.006 per cent. silicon and with stirring not resorted to at all.

Drown's method, silicon lost. Per cent.	Writer's method, silicon lost. Per cent.	Swedish method, silicon lost. Per cent.
0.018	0.016	0.002
0.012	0.028	0.000
0.018	0.018	0.002
0.020	0.028	0.006
0.016	0.026	0.000
0.022	0.020	0.006
0.012	....	0.006
0.034	....	0.012
0.012	....	0.008
0.014	....	....
0.018	0.028	0.006
0.018	0.022	0.000
0.028	0.022	0.000
0.012	0.034	0.012
0.032	....	0.006
0.024	....	0.006
0.018	....	0.006
0.010	....	0.004
0.030	....	0.002
0.020	....	....

The silicon percentages in these steels ranged from 0.15 to 0.25. Silicon lost in each case was determined by evaporating the filtrate. All evaporations were to dense fumes. The Swedish method seems to be in use in but a comparatively few (though large and important) laboratories, but for steel analysis deserves a wider popularity. In the case of high carbon steels the liquid in a covered dish may be boiled down rapidly on a thin steel plate, heated by a full Bunsen flame, to the end of the operation

[1] Hydrochloric acid doubtless serves as well.

without lowering the flame.[1] However the dehydration is just as complete when evaporated slowly.

The writer uses 50 cc. of dilute sulphuric acid (1 : 4) for 2.351 grams drillings steel, and observes that solution is complete before the sulphuric acid becomes concentrated. But in the determinations of silicon in steel given by Drown's method in the first table the proportion of sulphuric acid used was for part of them 10 cc. concentrated acid to 1 gram drillings and for the remainder 3.5 cc. per gram drillings. The following results from a 3.55 per cent. silicon pig iron show that in pig iron analysis as regards the point under discussion Drown's method is as effective as the old Swedish.

Drown: silicon lost, per cent, 0.168, 0.14, 0.14, 0.164, 0.133, 0.152
Swedish " " " " 0.096, 0.096, 0.096

That these losses are due not to the iron sulphate protecting the silicic acid, but to the cause already referred to in a foot-note, is shown by the results of a number of tests made by the Swedish method and with five minutes' stirring after appearance of fumes in which the respective losses were 0.152 per cent. and 0.112 per cent. silicon; and also by another test by the Swedish method, in which two evaporations were made before filtration and in which the loss was 0.108 per cent. silicon. Incidentally it is shown by these and the above tests that the hydrofluoric acid treatment usually insisted upon should not be included in a silicon determination, unless the silica remaining in the filtrate be recovered or allowed for. The same is, of course, true also of ferrosilicons.

The following results from different ferrosilicons give some hint of the proportion these mutually opposing errors are apt to bear to each other.

The silica lost is about 3 per cent. of the total as usual. The hydrofluoric acid residues seem to be apt to run somewhat less.

Silicon lost, per cent.....0.43, 0.23
H. F. residues, per cent.....0.16, 0.24, 0.14

In the following table total silicon (silicon as usual plus silicon in filtrate) results by the Swedish method are compared with total silicon results by Drown's method.

[1] An impossible operation in Drown's method; impossible also, usually, in this method, in the case of low carbon steels and wrought irons. For such, it is perhaps better to use hydrochloric acid instead of sulphuric.

Steel.	Drown's method. Per cent.	Swedish method. Per cent.
A	0.190	0.190
"	0.190	0.196
"	0.196	....
"	0.192	....
B	0.178	0.184
"	0.178	0.182
"	0.182	....
"	0.190	....
C	0.204	0.202
"	0.202	0.204
"	0.202	0.200

LABORATORY OF HENRY DISSTON & SONS' STEEL WORKS, PHILADELPHIA.

ON THE DECOMPOSITION OF THE CHLORIDES OF ALKALI METALS.

By C. W. VOLNEY.

Received February 23, 1901.

PART I.

THE action of sulphuric acid on the chlorides of the alkali metals is usually expressed by

$$RCl + H_2SO_4 = RHSO_4 + HCl.$$

It has been observed that concentrated sulphuric acid acts with considerable violence on the alkaline chlorides at the common temperature; that an acid, which has been diluted with one-quarter or one-third of its weight of water, acts with less violence, developing hydrochloric acid gas on the application of heat; and it is known that, if less acid than as above is used, the hydrochloric acid gas is developed only on applying considerable heat. Thus we observe that in the manufacture of sulphate by the Leblanc process, 2 molecules of salt are used with 1 molecule of sulphuric acid (60° Bé) and that, whereas, only about 70 per cent. of the hydrochloric acid gas is driven off in the pans, the mass has further to be calcined at a high temperature in the calcining furnaces, to complete the decomposition. We have, therefore, *a priori* to conclude that, in order to effect a thorough decomposition of the chloride by sulphuric acid, the application of heat is necessary; that the decomposition takes place periodically, as the temperature is raised, and that it is generally presumed that

the entire decomposition is effected at a lower temperature when the materials are used in quantities corresponding with

$$NaCl + H_2SO_4 = NaHSO_4 + HCl$$

than with

$$2(NaCl) + H_2SO_4 = Na_2SO_4 + 2HCl.$$

But it may be stated here that the operation does not take place quite in accord with this theory. If we bring concentrated sulphuric acid in contact with sodium chloride at the common temperature, the action takes place at once; the mass foams under development of hydrochloric acid gas, and ultimately ceases. When the quantities used correspond with the bisulphate formulation, a considerable portion of the gas is driven out, but hardly one-half of the theoretical quantity. If the mass is not heated, the process is ended, so that even with sufficient acid to form the bisulphate, only about one-half of the chloride is decomposed; the other half can be decomposed only by the application of heat.

For the purpose of investigating this matter, I undertook first to determine the quantity of hydrochloric acid gas, which is developed during the indicated phases of the process.

I effected the decomposition of the chlorides in an apparatus very much like those usually described for the preparation of hydrochloric acid. As the mass foams very much, when concentrated acid is used, the flask is of ample proportion and provided with a thermometer, safety funnel, and gas delivery tube. Between the absorption vessel and the development flask I inserted an empty bottle with safety tube, serving as receiver of substances carried over from the flask, and also as a safety valve.

At each phase I drew through the apparatus a sufficient quantity of air, to carry the gas from the apparatus into the absorbing water. An aliquot portion of the solution of hydrochloric acid gas in water served for the determination of hydrochloric acid by normal soda solution. In this process, equivalent proportions of the chlorides and sulphuric acid in grams were used.

The temperatures in the flask during the periods of gas development were noted.

1. DECOMPOSITION OF SODIUM CHLORIDE.

To 117 grams sodium chloride, 200 grams sulphuric acid (sp. gr. 1.84) were added.

The evolution of gas is violent; the mass foams. Temperature,

18°. No rise of temperature is observed. In the absorption vessel was a liter of water, of which, after the reactions were finished, aliquot portions (100 cc.) were used for the determination of hydrochloric acid.

It was found that the flask, containing the salt and sulphuric acid, should be frequently shaken to effect the reaction, otherwise only an imperfect decomposition of the chloride takes place. This is shown by the following two series of determinations, one resulting from the flask left at rest, and the other frequently shaken. From 117 grams sodium chloride, one-half of the theoretical quantity of HCl (73), that is, 36.5 grams, should be set free and found in the absorbing water:

	Percentages found.	
	I.	II.
	26.49	33.58
	25.91	32.12
	27.61	34.31
	26.50	33.58
	26.50	34.42
	27.31	33.60
	26.00	34.12
	....	34.30
Average	26.6	33.7

Theoretical amount, 36.5.

This shows that 95 per cent. of the theoretical amount of hydrochloric acid has been developed; and that only 46 per cent. of the total amount of the acid has been set free at the common temperature by an excess of sulphuric acid.

The residue in the flask solidifies almost entirely to a salt cake, when left for a length of time undisturbed. Shortly after the gas development ceases, it shows a mixture of an oily liquid with undecomposed sodium chloride, and in the liquid, needles of crystallization begin to form. If at this time the liquid is poured off from the forming salt cake and filtered, crystals are obtained, which show the composition $NaH_3.2SO_4$, and as it appears somewhat difficult to effect a separation of these crystals from the remaining sodium chloride and free sulphuric acid, I will describe an improvement on the filtering apparatus, which I have used on former occasions for similar purposes.[1] The bell-jar was connected with a Woulfe bottle containing sulphuric acid in such

[1] This Journal, **23**, 490.

a way as to admit dry air to the jar through a tube with stop-cock.

The liquid or salt mixture is poured on a platinum cone, which is finely perforated, and placed into the funnel of the filtering apparatus, which is placed into the bell-jar. When the air is exhausted, the faucet is opened sufficiently to let a very slow stream of air pass through the apparatus. This air is dried by sulphuric acid. By means of this filtration in a vacuum, the superfluous sulphuric acid is removed from the crystals on the platinum cone, and, as I have found by comparative tests, the salt on the filter may be washed with concentrated sulphuric acid to remove any traces of sodium chloride, without changing the crystallization on the filter. This is owing to the fact that the polysulphates, formed in the salt cake of the flask, are not affected by concentrated sulphuric acid. In this manner material for analysis was obtained, and the parts of the salt crystallizing from sulphuric acid, or from the oily liquid in the flask before solidifying, gave, on analysis, the following results:

	Found.				Theory for $NaH_3(SO_4)_2$.
	I.	II.	III.	Average.	
Na.....	9.31	....	8.100	8.70	10.550
H_3.....	2.11	11.8	1.6	1.85[1]	1.376
SO_4.....	87.50	89.9	92.3	89.9	88.073
	98.92	101.7	102.00	100.45	99.999

The irregularities in these results the writer can ascribe only to the difficulty in separating the different salts, which necessarily existin the mixture. From the foregoing, I conclude that the action of concentrated sulphuric acid on sodium chloride at 18° can be expressed thus:

$$2NaCl + 2H_2SO_4 = NaH_3(SO_4)_2 + HCl + NaCl.$$

This reaction takes place without any development of heat, and with its termination the development of hydrochloric acid gas ceases.

The second period of the development of the gas commences when heat is applied to the mass. From the fact that gas develops as soon as the flask becomes warm, and that the salt cake in the flask melts easily, and the gas development continues until the cake becomes hard and dry, the reaction may be considered

[1] Omitting II.

as taking place between the polysulphate and the remaining sodium chloride and may be expressed thus:

$$NaH_3(SO_4)_2 + NaCl = 2NaHSO_4 + HCl.$$

The mass in the flask showed, at the end of this part of the process, nearly 120°. The salt cake is now the usual bisulphate. The hydrochloric acid gas absorbed in the same manner as described in the first part of the process, measured by titration with normal alkali, corresponds within from 2 to 7 per cent. in excess with the calculation. This great difference is evidently owing to the fact that quantities of the sodium chloride escape contact with the sulphuric acid, in the measure, as the salt cake becomes thick or solid. The difficulties in the practical manipulation in this investigation consist mainly in the impossibility, so far, of separating the trihydrogen sodium disulphate from the remaining sodium chloride, or from any other sulphates, which may be formed during the first period or phase of the action of the sulphuric acid on the chloride. On contact with atmospheric air, water is very quickly absorbed by the liquid and also by the polysulphates, and the result is then always sodium bisulphate and diluted sulphuric acid.

2. DECOMPOSITION OF POTASSIUM AND AMMONIUM CHLORIDES.

In the continuation of the experimental part of this investigation, the action of concentrated sulphuric acid on potassium chloride and ammonium chloride, during the first phase of the reaction, has been examined. The quantities brought in contact at the common temperature, 17°–18°, complied with $RCl + H_2SO_4$. The temperature of the mixture of potassium chloride and acid remains stationary until the acid has come well in contact with the chloride, when the temperature rises from 17° to 30°, receding again to 17° after the corresponding reaction is finished. When sulphuric acid reacts on ammonium chloride under the same conditions, the temperature falls quickly from 18° to 1°.

This work is to be continued.

Reference to Literature:
Carl Schultz: "Ueber saure Salze der Schwefelsäure," Pogg. *Ann.*, 1868.

QUANTITATIVE DETERMINATION OF FLUORINE IN FLUORIDES EASILY DECOMPOSABLE BY SULPHURIC ACID.[1]

By W. E. Burk.

Received September 3, 1901.

IN determining the purity of commercial fluorite, two methods were found outlined which appealed as practicable, one described by Hillebrand,[2] based upon the method of Rose, and the one of M. Carnot described at length in a paper "Sur le dosage du fluor."[3]

A modification of Carnot's method, as recommended by Cairns, was tried but with little success.

The method described by Hillebrand, while satisfactory for complex silicates, was not found as suitable as that of Carnot, and a modification of the latter with certain precautionary additions was adopted with satisfactory results. Without these additional precautions, however, the method does not give accurate results, but invariably shows too high percentage of fluorine.

The method adopted is as follows:

A perfectly dry mixture of about 3 grams of dry powdered and calcined silicon dioxide and 0.20 gram of dry powdered fluorite with 40 cc. concentrated sulphuric acid is digested at a temperature of 120° to 135°, the silicon tetrafluoride evolved being conducted through a perfectly dry conducting tube to a narrow upright vessel containing about 20 cc. of a freshly prepared 10 per cent. solution of potassium fluoride. The end of the conducting tube dips into a sufficient pool of pure mercury to prevent moisture from entering the tube. A slow current of dry air is passed while the temperature of the sulphuric acid mixture is maintained for one and a half hours.

The reactions involved are as follows:

$$CaF_2 + H_2SO_4 = 2HF + CaSO_4;$$
$$4HF + SiO_2 = SiF_4 + 2H_2O.$$

In the receiving vessel:

$$SiF_4 + 2KF = K_2SiF_6.$$

The potassium fluosilicate separates out partially, and after

[1] This paper is an extract from a portion of a thesis presented to the Rose Polytechnic Institute for the Master's degree.

[2] Bulletin 176 of U. S. Geological Survey.

[3] *Compt. rend.*, 114, 750 (1892).

transferring to a subsiding vessel and adding an equal volume of 90 per cent. alcohol it subsides perfectly to a heavy pulpy stratum. After a half hour the contents are filtered, using a Gooch crucible with asbestos plate, washed free from potassium fluoride with 90 per cent. alcohol and dried to constant weight at a temperature of 100° C. Two-thirds of the fluorine of the potassium fluosilicate comes from the fluorite, or the weight of the salt, multiplied by the factor 0.34511, gives fluorine; and this multiplied by 2.0527 gives the calcium fluoride.

The detail manipulation must be followed with great care, in which case only will satisfactory results be obtained. The three chief sources of error are:

1. Moisture in air current or conducting tubes, resulting in premature decomposition of the silicon tetrafluoride in the tubes and even clogging of the tubes.

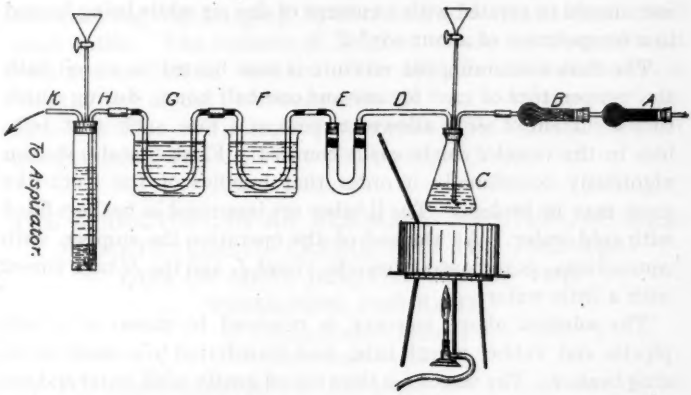
2. Sulphuric acid fumes carried over by a current of air, resulting in the decomposition of the potassium fluoride of the solution in the receiving vessel and the formation of potassium fluosilicate with consequent high percentage determination.

3. Flakes of insoluble addition products of potassium fluoride of the solution with silicon dioxide of the walls of the glass (where used) receiving vessel. A 10 per cent. solution of potassium fluoride attacks glass quite readily and high percentage is usual from this source unless great care is taken.

These sources of error are so serious that early in the experimental work, while using a sample of rather pure fluorite, containing 98.77 per cent. calcium fluoride, values as high as in one case 130 per cent. calcium fluoride, and in another 113 per cent. calcium fluoride were obtained.

Details of the method are as follows, in which statements and references are made to the accompanying sketch of apparatus:

Tube *A* contains glass wool saturated with concentrated sulphuric acid and tube *B* contains fused calcium chloride. From these drying tubes a conducting glass tube extends to the bottom of vessel *C*, which is an Erlenmeyer flask of 150 cc. capacity, closed with a three-holed rubber stopper, the second and third holes of which are closed with a stop-cock funnel and a glass tube *D*, one end of which terminates just below the rubber stopper, the other end of the tube projecting into a U-tube, *E*, plugged at points indicated by cross hatching with pure glass wool. *F* and *G* are



U-loops bent from 5 mm. glass tubing, connected with tight rubber joints and plugged with glass wool at the points indicated, the plugs being designed to interrupt the current of air and effect a stoppage of sulphuric acid fumes which are not otherwise eliminated. *H* is a glass tube extending to the bottom of the vessel *I*, and terminating in a contracted end bent upward. Into the containing vessel *I* is placed sufficient pure dry mercury to seal the opening of the tube *H* by 2 mm. to 3 mm. at least. Vessel *I* is closed with a three-holed rubber stopper, through which a stop-cock funnel, and the tube *K* enter.

Tube *K* leads to an aspirator. The conducting tubing from *C* to *H* measures in length some 2 meters and contains in all 7 plugs of glass wool. Each part of the apparatus is dried by warming and exhausting the air before the apparatus is set up. After the apparatus is adjusted, a current of air is allowed to pass while the parts are again heated with a naked flame. The current of air is now stopped and about 20 cc. of a freshly prepared solution of potassium fluoride (10 per cent.) are poured into the vessel *I* by means of a funnel.

Three grams of pure powdered silicon dioxide are calcined and, while still slightly warm, are intimately mixed in an agate mortar with 0.20 gram of the fluorite, which has been powdered and thoroughly dried. This mixture is transferred to the flask *C* and the same immediately closed. Forty cc. concentrated sulphuric acid are now added through the stop-cock funnel. This acid, before

use, should be aerated with a current of dry air while being heated to a temperature of about 165° C.

The flask containing the mixture is now heated in an oil-bath at a temperature of 120° for one and one-half hours, during which time a current of air is allowed to pass at a rate such that bubbles in the vessel *I* can be easily counted. Flask *C* is also shaken vigorously occasionally in order that bubbles of the froth-like scum may be broken. The U-tubes are immersed in beakers filled with cold water. At the end of the operation the stopper, with connections, is removed from the vessel *I*, and the *H* tube rinsed with a little water.

The solution above mercury is removed by means of a bulb pipette and rubber mouth tube, and transferred to a small subsiding beaker. The vessel *I* is then rinsed gently with water and the mercury washed. As little water is used in washing as possible, the solution and rinsings being kept down within 75 cc. A thin, somewhat tenacious coating on the inner wall of the vessel *I* should not be removed, as this is due to addition-products of the potassium fluoride of solution with the glass. Care is also taken that no minute globules of mercury are transferred to the beaker. An equal volume of 90 per cent. alcohol is now added and the beaker allowed to stand to perfect subsidence. Decant and filter through a Gooch filter with reduced pressure. The subsiding vessel should be rinsed well though not rubbed. A tared crucible with asbestos plate is used, and after filtering, the contents are washed with 90 per cent. alcohol till the filtrate gives no turbidity with barium chloride. The crucible and contents are now dried at 100° C. in a hot air oven to constant weight, and fluorine or calcium fluoride estimated.

M. Moissan, in a paper on his investigations of fluorine,[1] mentions the decided tendency of fluorine and its simple compounds to form addition-products. This action, constituting the third chief source of error above mentioned, could be best eliminated by the use of platinum for the vessel *I*, and with this substitution the method would be very satisfactory. Platinum could be used with equal satisfaction and much economy of time for the conducting tubes from vessel *C* to vessel *I*.

The modification of Carnot's method as proposed by Cairns consists in using potassium chloride instead of potassium fluoride,

[1] Annual report of the Smithsonian Institution for 1897.

and catching any escaping hydrochloric acid gas in a connected wash-bottle. The contents of the two vessels are then titrated with standard alkali solution. The objection to this method is that the end of the titration reaction is very indefinite and indeterminate, due to a secondary reaction. (See "Grundlinien der anorganischen Chemie," Ostwald, pp. 433–436.)

THE REDUCTION, IN AN ALKALINE SOLUTION, OF 2,4,5-TRIMETHYLBENZALAZINE AND THE PREPARATION OF SOME DERIVATIVES OF THE REDUCTION PRODUCTS.

By Everhart Percy Harding.

Received September 9, 1901.

THE experimental part of this paper was carried out in the chemical laboratory at the University of Heidelberg under the supervision of Prof. Curtius, and a short abstract of it has already been published in the July, 1900, number of the *Journal für praktische Chemie.*

The formation of azines by the condensation of aromatic aldehydes with hydrazine and their reduction in an acid or alkaline solution is a comparatively new line of work and the investigation along this line has largely been done by Prof. Curtius and his students at the University of Heidelberg.

2,4,5-Trimethylbenzalazine, $(CH_3)_3C_6H_2CH{:}N.N{:}CHC_6H_2(CH_3)_3$, yields different reduction products, the kind depending upon the quality of the reducing agent used and the degree of the reduction. Curtius and Franzen,[1] by reducing in an acid solution, using zinc dust and acetic acid, obtained 2,4,5-trimethyldibenzylamine, a solid substance melting at 78° and insoluble in water. The reaction may be represented by the equation

$$(CH_3)_3C_6H_2CH{:}N.N{:}CHC_6H_2(CH_3)_3 + 3H_2 = \begin{matrix}(CH_3)_3C_6H_2CH_2\\(CH_3)_3C_6H_2CH_2\end{matrix}\!\!>\!NH + NH_3,$$

2,4,5-Trimethyldibenzylamine

part of the nitrogen being reduced to ammonia.

By reducing 2,4,5-trimethylbenzalazine in an alkaline solution, using sodium amalgam as a reducing agent, two reduction prod-

[1] *Ber. d. chem. Ges.*, 4, 1901.

ucts were obtained, the kind depending upon the degree of reduction — one a 2,4,5-trimethylbenzal-2,4,5-trimethylbenzylhydrazone, $(CH_3)_3C_6H_2CH_2NH.N:CHC_6H_2(CH_3)_3$, produced by a partial reduction, the other a symmetrical 2,4,5-trimethyldibenzylhydrazine, $(CH_3)_3C_6H_2CH_2.NH.NH.CH_2C_6H_2(CH_3)_3$, produced by a complete reduction. The reactions may be represented by the following equations:

$$(CH_3)_3C_6H_2CH:N.N:CHC_6H_2(CH_3)_3 + H_2 = (CH_3)_3C_6H_2CH_2.NH.N:CHC_6H_2(CH_3)_3$$

2,4,5-trimethylbenzal-2,4,5-trimethylbenzylhydrazone

and

$$(CH_3)_3C_6H_2CH:N.N:CH.C_6H_2(CH_3)_3 + 2H_2 = (CH_3)_3C_6H_2CH_2.NH.N:CH.C_6H_2(CH_3)_3.$$

Symmetrical 2,4,5-trimethyldibenzylhydrazine.

The symmetrical hydrazine may be obtained also from the hydrazone by a further reduction.

$$(CH_3)_3C_6H_2CH_2.NH.N:CH.C_6H_2(CH_3)_3 + H_2 = (CH_3)_3C_6H_2CH_2.NH.NH.CH_2C_6H_2(CH_3)_3.$$

Each of these reduction products is a solid substance and comparatively unstable.

The azines are aliphatic compounds, derivatives of the hypothetical azimethylene —CH.N.N.CH—, and by a partial reduction one would expect a symmetrical reduction product—either a hydrazymethylene derivative, =CH.NH.NH.CH=, in which the valence of nitrogen has changed from III to V or an azomethane derivative corresponding to the aromatic azo compounds and having the general formula $R—CH_2.N:N.CH_2—R$. But this is not the case as is evidenced by the decomposition products which show an unsymmetrical reduction, the compounds having the general formula $R—CH_2.NH.N:CH—R$. By hydrolyzing the hydrazones with dilute hydrochloric acid they form an aldehyde and a substituted hydrazine, which reaction is best explained by the hydrazone or unsymmetrical formula

$$RCH_2.NH.N:\overset{H_2}{\underset{}{|}}CHR\overset{}{\underset{O}{|}}$$

The formation of but one acetyl or benzoyl derivative favors the presence of but one imide group or one methylene group as exist in the unsymmetrical hydrazone while the two imide groups in the assumed hydrazimethylene derivative or the two methylene

groups in the assumed azimethane derivatives would make a diacetyl or dibenzoyl derivative probable.

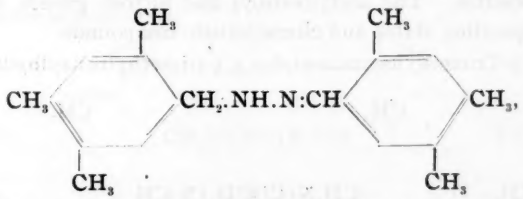
The symmetrical hydrazines produced by a complete reduction of the azines in an alkaline solution are also aliphatic compounds, derivatives of hydrazomethane, $R—CH_2NH.NH.CH_2—R$, which correspond to the aromatic hydrazo compounds $R—NH.NH—R$. The latter are easily reduced to primary amines while the former are stable in an alkaline solution. No attempt has been made to reduce the symmetrical hydrazine in an acid solution but the probability is that in the preparation of the secondary amines $\begin{matrix} R—CH_2 \\ R—CH_2 \end{matrix}\!\!>\!NH$, by the reduction of the azines in an acid solution, the symmetrical hydrazine forms as an intermediate product and then reduces further to one molecule of ammonia and one molecule of a secondary amine instead of to two molecules of a primary amine as do the aromatic hydrazo compounds, the final reaction taking place according to the equation

$$R—CH_2.NH.NH.CH_2—R + H_2 = NH_3 + \begin{matrix} R—CH_2 \\ R—CH_2 \end{matrix}\!\!>\!NH,$$

instead of the equation

$$R—CH_2.NH.NH.CH_2—R + H_2 = 2RCH_2NH_2.$$

To make 2,4,5-trimethylbenzal-2,4,5-trimethylbenzylhydrazone,



10 grams of 2,4,5-trimethylbenzalazine were placed in a round bottomed flask, of 1 liter capacity, which was provided with a reflux condenser. This was dissolved in 700 cc. of 95 per cent. alcohol by boiling vigorously on a water-bath. To the solution which was kept at the boiling-point of the alcohol there was added, intermittently, aliquot parts of 300 grams of sodium amalgam, more than a sufficient amount to reduce the azine to the hydrazone. After an interval of four hours the amalgam had

become spent and the solution nearly colorless, maintaining a slight turbidity. The mercury and impurities were filtered off and the filtrate placed in a refrigerator. In twelve hours' time 4 grams of a flaky, white, crystalline substance had separated out, which was filtered off and well washed with water. From a dilute alcoholic solution, needle-like crystals formed, while from a concentrated alcoholic solution the crystals grouped themselves in the form of tufts which melted at 134°.

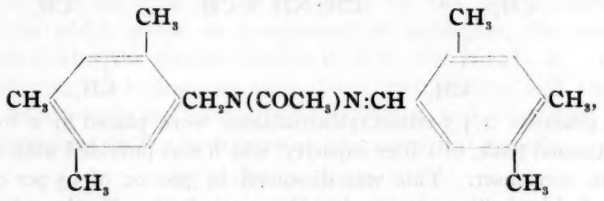
An analysis gave:

	Theoretical. Per cent.	Found. Per cent.
Carbon	81.63	81.85
Hydrogen	8.57	8.84
Nitrogen	9.36	9.53

The molecular weight, determined by the depression of the freezing-point method, was found to be 311 and 309.7 as against 294 the theoretical molecular weight. The hydrazone is very soluble in ether and ligroin, less soluble in alcohol and acetic acid, and insoluble in water. On exposure to the air it soon decomposes, assuming a yellow color and emitting an odor of pseudocumylaldehyde. It is unstable in an exhausted desiccator and is readily decomposed by the action of steam or hydrochloric acid.

The replaceable imide hydrogen atom makes substitution products possible. The acetylbenzoyl and nitroso groups form the corresponding stable and characteristic compounds.

2,4,5-Trimethylbenzalacetyl-2,4,5-trimethylbenzylhydrazone,

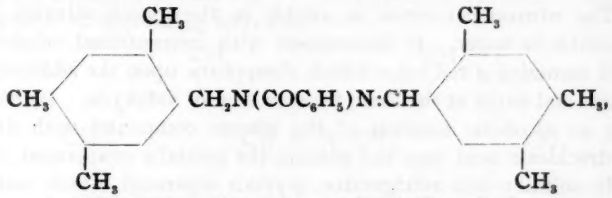


was formed by treating a concentrated and hot alcoholic solution of the hydrazone with an excess of acetic anhydride and the excess evaporated off on a water-bath. Recrystallized from alcohol the long fine needles melted at 184°. An analysis gave:

	Theoretical. Per cent.	Found. Per cent.
Carbon	78.57	78.50
Hydrogen	8.33	8.36
Nitrogen	8.34	8.54
Oxygen	4.76	4.60

It is soluble in the organic solvents and insoluble in water.

The benzoyl derivative,



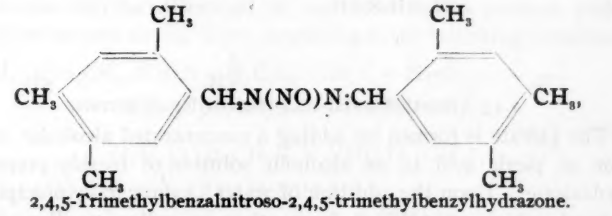
2,4,5-Trimethylbenzalbenzoyl-2,4,5-trimethylbenzylhydrazone.

was easily prepared by the Schotten-Baumann reaction. An analysis gave:

	Theoretical. Per cent.	Found. Per cent.
Carbon	81.41	81.48
Hydrogen	7.54	8.11
Nitrogen	7.03	6.89
Oxygen	4.02	3.52

It crystallizes from alcohol in fine needle-like crystals which melt at 187°. It is soluble in the organic solvents and insoluble in water.

The nitroso derivative,



2,4,5-Trimethylbenzalnitroso-2,4,5-trimethylbenzylhydrazone.

was prepared by adding to an ice-cold mixture of alcohol and hydrazone, concentrated hydrochloric acid, drop by drop, until the hydrazone dissolves. An ice-cold concentrated solution of sodium nitrite was then gradually added. A yellow crystalline substance separated at once, which increased upon the addition of water to the solution. The precipitate was filtered off and

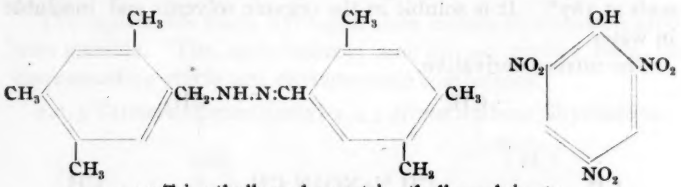
well washed with water to remove excess of sodium nitrite. Recrystallized from alcohol, the yellow needles melted at 118°.

An analysis gave:

	Theoretical. Per cent.	Found. Per cent.
Carbon	74.31	74.13
Hydrogen	7.74	8.27
Nitrogen	13.00	13.28
Oxygen	4.95	3.32

The nitroso derivative is soluble in the organic solvents and insoluble in water. It decomposes with concentrated sulphuric acid assuming a red color which disappears upon the addition of water and emits at the same time an odor of aldehyde. By treating an alcoholic solution of the nitroso compound with dried hydrochloric acid gas and placing the partially evaporated alcoholic solution in a refrigerator, crystals separated which melted at 155°–156°. This compound appeared to be a hydrochloride of the nitrosohydrazone, for by treating it with sodium hydroxide it formed the hydrazone melting at 134° and by treating with sodium nitrite it formed again the nitroso compound melting at 118°. In preparing the nitroso compound, the temperature must be kept near the freezing-point or the derivative will decompose.

The hydrazone is a weak base. With dilute organic acids it forms addition products, the molecule remaining intact at the double bond. With picric acid it forms a hydrazone picrate.



2,4,5-Trimethylbenzal-2,4,5-trimethylbenzylpicrate.

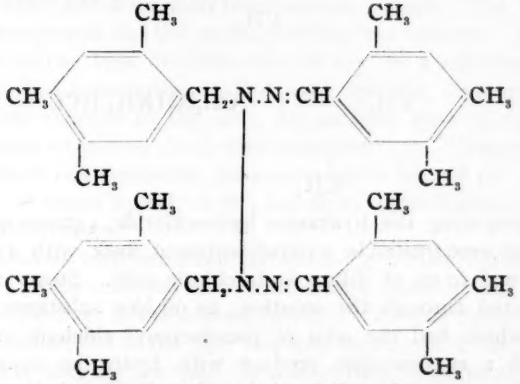
The picrate is formed by adding a concentrated alcoholic solution of picric acid to an alcoholic solution of freshly prepared hydrazone. Upon the addition of water a yellow flaky precipitate formed, which crystallized from ether in yellow needles which melted at 169°. An analysis gave:

	Theoretical. Per cent.	Found. Per cent.
Carbon	59.66	59.73
Hydrogen	5.54	5.16
Nitrogen	13.39	13.52
Oxygen	21.41	21.59

The picrate is insoluble in water and difficultly soluble in the organic solvents.

Curtius and his students[1] succeeded in preparing from benzalbenzylhydrazone, 4-methylbenzal-4-methylbenzylhydrazone and 2,4-dimethylbenzal-2,4-dimethylbenzylhydrazone, respectively, the corresponding tetrazones, by oxidizing with mercuric oxide.

2,4,5-Trimethylbenzal-2,4,5-trimethylbenzylhydrazone failed to give a corresponding tetrazone.



2,4,5-Trimethylbenzal-2,4,5-trimethylbenzyltetrazone.

Several trials were made modifying the method of the foregoing investigator but either the unchanged hydrazone remained or 2,4,5-trimethylbenzalazine was formed. It is assumed that the tetrazone may have formed as an intermediate product which oxidized at once to the azine according to the following equations:

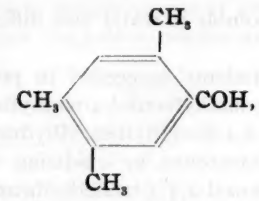
$$(CH_3)_3C_6H_2CH_2.NH.N{:}CH.C_6H_2(CH_3)_3 + HgO =$$
$$\left.\begin{matrix}(CH_3)_3C_6H_2CH_2N.N{:}CHC_6H_2(CH_3)_3\\ |\\ (CH_3)_3C_6H_2CH_2N.N{:}CHC_6H_2(CH_3)_3\end{matrix}\right. + H_2O + Hg.$$

$$\left.\begin{matrix}(CH_3)_3C_6H_2CH_2.N.N{:}CHC_6H_2(CH_3)_3\\ |\\ (CH_3)_3C_6H_2CH_2.N.N{:}CHC_6H_2(CH_3)_3\end{matrix}\right. + HgO =$$
$$2(CH_3)_3C_6H_2CH{:}N.N{:}CHC_6H_2(CH_3)_3 + H_2O + Hg.$$

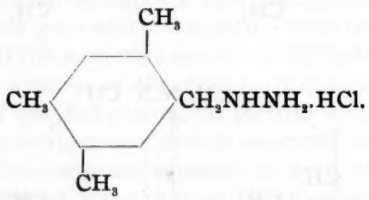
2,4,5-trimethylbenzalazine.

By the action of dilute hydrochloric acid the hydrazone hydrolyzes into 2,4,5-trimethylbenzaldehyde,

[1] *J. prakt. Chem.*, N. F., **62**, (1900).



and 2,4,5-trimethylbenzalhydrazine hydrochloride,

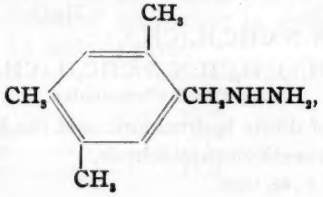


In preparing the hydrazine hydrochloride, 4 grams of the hydrazone were treated in a round-bottomed flask with 150 cc. of water and 10 cc. of dilute hydrochloric acid. Steam was then conducted through the solution; an oil-like substance distilled over which had the odor of pseudocumyl aldehyde and which formed a condensation product with hydrazine hydrate that melted at 180°, the melting-point of 2,4,5-trimethylbenzalazine. The hot residue in the flask was filtered and the filtrate distilled in a vacuum. The residue, recrystallized from alcohol, melted at 240°. An analysis gave:

	Theoretical. Per cent.	Found. Per cent.
Carbon	59.85	59.78
Hydrogen	8.51	8.47
Nitrogen	14.11	13.97
Chlorine	17.60	17.71

The hydrochloride is a very stable compound. It is soluble in water and insoluble in ether.

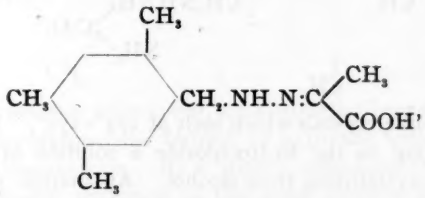
The free base 2,4,5-trimethylbenzylhydrazine,



was prepared from the hydrochloride by the action of caustic potash. Four grams of the hydrochloride and an excess of caustic potash were placed into an Erlenmeyer flask. A few drops of water were added and subsequently 50 cc. of ether. The flask was provided with a soda-lime tube to protect the base from the moisture and carbon dioxide of the atmosphere. The flask was shaken at times so as to bring the hydrochloride in contact with the potash. After twenty-four hours the ether was separated from the water layer and dried with fused caustic potash. The ether was then evaporated and the residue distilled in a vacuum. At 25 mm. pressure the base distilled over at 165° as a colorless oil, which solidified upon cooling. It is very unstable, decomposing at once when exposed to the air. An analysis gave 16.89 per cent. nitrogen as against 17.08 theoretical per cent. Upon standing three days in a desiccator, an analysis gave but 5.8 per cent. nitrogen. It began to melt at 78°, and at 85° there began a rapid evolution of nitrogen.

The base forms, with benzaldehyde benzal-2,4,5-trimethylbenzylhydrazone, a very unstable compound which melts at 89°–90°, and which dissolves in the organic solvents. It was formed by adding benzaldehyde to the free base and then rubbing the walls of the beaker with a glass rod. It was purified by crystallizing from alcohol.

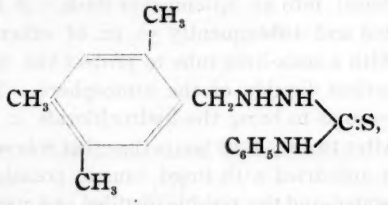
With pyroracemic acid the base forms 2,4,5-trimethylbenzylhydrazonepyroracemate,



a white crystallized substance which melted at 92°. It was prepared by adding an excess of pyroracemic acid to the hydrochloride of the base. An oil immediately formed which settled to the bottom of the flask and then crystallized. An analysis gave 11.79 per cent. of nitrogen as against 11.97 theoretical per cent. It is soluble in water and the organic solvents.

The base, 2,4,5-trimethylbenzylhydrazine, forms addition

products. With phenyl mustard oil it forms 2,4,5-trimethylbenzylphenylthiosemicarbazide,

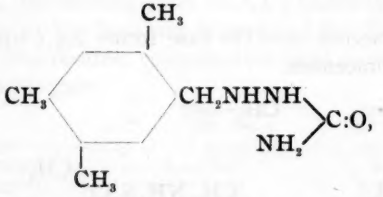


white hair-like crystals which melt at 167°–168°. It was prepared by adding to an alkaline solution of the base an excess of phenyl mustard oil, and then warming the solution. By warming at too high a temperature or with an excess of alkali the thiosemicarbazide decomposed and a black lustrous crystalline substance formed. An analysis gave:

	Theoretical.	Found. I.	II.
Nitrogen	14.09	14.42	14.22

It is soluble in ethyl alcohol, methyl alcohol, ether, benzene, and acetic acid. It is difficultly soluble in ligroin and water.

With hydrocyanic acid, the base forms 2,4,5-trimethylbenzylsemicarbazide,

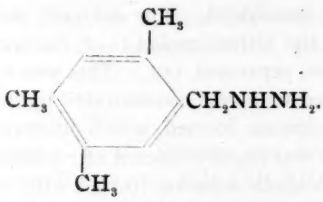


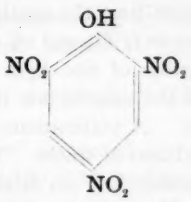
white needle-like crystals which melt at 174°–175°. It was prepared by adding to the hydrochloride a solution of potassium cyanate and crystallizing from alcohol. An analysis gave:

	Theoretical. Per cent.	Found. Per cent.
Nitrogen	20.29	20.47

It is easily soluble in ethyl alcohol, methyl alcohol, acetic acid, and benzene. It is difficultly soluble in water and insoluble in ether and ligroin.

With picric acid 2,4,5-trimethylbenzylhydrazine forms 2,4,5-trimethylbenzylhydrazine picrate.



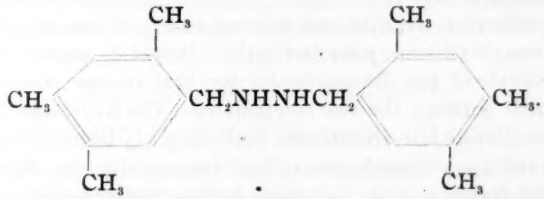


This addition product crystallizes in yellow needles which melt at 163°. In its preparation an ether solution of picric acid was gradually added to a water solution of the hydrochloride. The picrate formed at once as yellow crystals at the contact point of the two layers. By adding an ether solution of picric acid to a warm solution of the hydrochloride, the picrate formed as an oil, which settled to the bottom of the flask and subsequently crystallized. An analysis gave:

	Theoretical. Per cent.	Found. Per cent.
Nitrogen	17.81	17.64

It is difficultly soluble in warm water and insoluble in ligroin and benzene.

Preparation of symmetrical 2,4,5-trimethyldibenzylhydrazine,



As has previously been given, 2,4,5-trimethylbenzal-2,4,5-trimethylbenzylhydrazone was formed by a partial reduction of 2,4,5-trimethylbenzalazine. By a further reduction of the hydrazone or a stronger reduction of the azine solution the symmetrical 2,4,5-trimethyldibenzylhydrazone was formed. In the preparation of this compound 10 grams of 2,4,5-trimethylbenzalazine were dissolved in 500 cc. of 95 per cent. alcohol. To this warm solution in a round-bottomed flask provided with a reflux condenser was added, at times, aliquot parts of 300 grams of a 4 per cent. sodium amalgam. The solution was kept on a water-bath at the boiling-point of the alcohol for six hours dur-

ing which time the amalgam was added. The mercury and impurities were filtered off and the filtrate cooled in a refrigerator. Two grams of the hydrazone separated out. This was filtered off and the cold filtrate treated with cold concentrated hydrochloric acid. A voluminous precipitate formed which increased by the addition of water. This was rapidly filtered off, washed well with water and its dilute alcoholic solution treated with sodium hydroxide. A voluminous precipitate formed which, when recrystallized from alcohol, melted at 128°. An analysis gave:

	Theoretical. Per cent.	Found. Per cent.
Nitrogen	9.46	9.47

The molecular weight by the depression of the freezing-point method gave:

		Found.	
	Theoretical.	I.	II.
Mol. wt.	296	305.7	321

The free base cannot be obtained directly from the filtrate from the hydrazone. By evaporating the filtrate, the dibenzylhydrazine is oxidized to the hydrazone and by the addition of water to the filtrate the hydrazine decomposes. It is very unstable. It soon becomes a yellowish white, emitting an odor of 2,4,5-trimethylbenzaldehyde.

The molecular weights and melting-points of the hydrazone and dibenzylhydrazine vary but little. It was by means of the hydrochloride of the dibenzylhydrazine that it was possible to distinguish between the two compounds. The hydrazone forms no hydrochloride but decomposes, yielding 2,4,5-trimethylbenzaldehyde and 2,4,5-trimethylbenzylhydrazine while the dibenzylhydrazine forms a stable and characteristic hydrochloride which melts at 171°. In an alcoholic solution it soon decomposed, and by boiling the solution almost immediately.

2,4,5-trimethyldibenzylhydrazine, as was previously given, is an aliphatic compound, a symmetrical derivative of hydrazimethane, $CH_2NH.NHCH_2$, corresponding to the hydrazo compounds of the aromatic series. The aromatic hydrazo compounds oxidize very readily, the colorless hydrazobenzene oxidizing in a very short time to the red azobenzene by means of atmospheric oxygen. The corresponding aliphatic hydrazi compounds also oxidize readily but do not form the corresponding azo compounds. They form either symmetrical tetrazones with the general formula

$=N.N:N.N=$,[1] or oxidize first to the corresponding hydrazone and then to the unsymmetrical tetrazone with the general formula $\begin{matrix}-N-N:\\ |\\ -N-N:\end{matrix}$,[2] or to the azines with the general formula $-CH:N.N:CH-$.[2] Curtius and Franzen[3] succeeded in oxidizing dibenzylhydrazine, $C_6H_2CH_2.NH.NH.CH_2C_6H_5$, to dibenzyltetrazone and gave it the formula

$$\begin{matrix}C_6H_5CH_2\\ C_6H_5CH_2\end{matrix}\!\!>N.N:N.N<\!\!\begin{matrix}CH_2C_6H_5\\ CH_2C_6H_5\end{matrix}.$$

Curtius and Propfe attempted to obtain the symmetrical 4-methyldibenzyltetrazone, $(CH_3C_6H_4CH_2)_2N.N:N.N(CH_2C_6H_4CH_3)_2$, by oxidizing symmetrical 4-methyldibenzylhydrazine,

$$CH_3C_6H_4CH_2.NH.NH.CH_2C_6H_4CH_3,$$

but succeeded in obtaining the unsymmetrical 4-methylbenzal-4-methylbenzyltetrazone,

$$\begin{matrix}CH_3C_6H_3CH_2.N.N:CHC_6H_4CH_3\\ |\\ CH_3C_6H_2CH_2.N.N:CHC_6H_4CH_3\end{matrix}.$$

Likewise Curtius and Haagar,[4] in attempting to oxidize 2,4-dimethyldibenzylhydrazine, $(CH_3)_2C_6H_3CH_2NHNHCH_2C_6H_3(CH_3)_2$ to the symmetrical tetrazone, obtained the unsymmetrical 2,4-dimethylbenzal-2,4-dimethylbenzyltetrazone,

$$\begin{matrix}(CH_3)_2C_6H_3CH_2.N.N:CHC_6H_3(CH_3)_2\\ |\\ (CH_3)_2C_6H_3CH_2.N.N:CHC_6H_3(CH_3)_2\end{matrix}.$$

Neither the symmetrical nor unsymmetrical tetrazone could be isolated by oxidizing symmetrical 2,4,5-trimethyldibenzylhydrazine with mercuric oxide. Either or both of these compounds may have formed as intermediate products but the only compound that could be isolated after the oxidation was 2,4,5-trimethylbenzalazine.

Schmidt and Schulz[5] succeeded in substituting two acetyl groups for the two imide hydrogen atoms in the aromatic hydrazobenzene, thus forming a diacetyl derivative,

[1] *Ber. d. chem. Ges.*, **4**, 1901.
[2] *J. prakt. Chem.*, N. F., **62**, (1900).
[3] *Ber. d. chem. Ges.*, (1900).
[4] *J. prakt. Chem.*, N. F., **62**, (1900).
[5] *Ann. Chem.* (Liebig), **207**, 327.

$$C_6H_5N(COCH_3)-N(COCH_3)-C_6H_5.$$

The diacetyl, dibenzoyl, and dinitroso derivatives[1] of dibenzylhydrazine have been prepared. Also the dibenzoyl derivative[1] of 4-methyldibenzylhydrazine and the diacetyl derivative[1] of 2,4-dimethyldibenzylhydrazine.

None of the corresponding diderivatives of 2,4,5-trimethyldibenzylhydrazine have been prepared. In every trial a monoderivative of 2,4,5-trimethylbenzal-2,4,5-trimethylbenzylhydrazone was formed. It is assumed that the symmetrical hydrazine was oxidized to the hydrazone according to the equation

$$(CH_3)_3C_6H_2CH_2NHNHCH_2C_6H_2(CH_3)_3 + O = (CH_3)_3C_6H_2CH_2NHN{=}CHC_6H_2(CH_3)_3 + H_2O,$$

and that then a hydrogen atom of the imide group was replaced by one of the substituting radicals.

THE PRECIPITATION OF COLLOIDS BY ELECTROLYTES.

By W. R. Whitney and J. E. Ober.

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PART I.

REVIEW OF THE WORK OF PREVIOUS INVESTIGATORS.

THE purpose of this article is to call attention to the present condition of our knowledge concerning colloids by coordinating some of the facts and conceptions which have resulted from the work of various investigators in this field, and to append thereto a contribution to the subject, the result of recent experiments of our own together with a fairly complete index to the literature. It is hoped that the significance of this subject and its probable importance in connection with biological chemistry in its widest significance, as well as its claim to general chemical interest, may be brought more fully to the attention of chemists.

Any discussion of the subject which considers its history must begin with a reference to the work of Graham. He distinguished

[1] *J. prakt. Chem.*, N. F., **62** (1900).

a new class of substances which exhibit little or no chemical affinity, which do not crystallize, which dissolve in various solvents apparently without any limiting solubility therein, which exhibit little or no tendency to diffuse when in solution, and which may be filtered from their solutions by animal membranes or parchment. These substances also exhibit the property of gelatinization or coagulation, the change often being spontaneous or brought about or catalyzed simply by the presence of acids, salts, etc. Graham gave the name colloid to this class of substances and called their solutions in water, alcohol, etc., hydrosols, alcosols, etc., while the names hydrogel, alcogel, etc., were given to the coagulum. He recognized that both organic and inorganic substances existed in these forms, and there were thus classified together such chemically different materials as silicic acid, ferric hydroxide, and gelatine.

The application by van't Hoff of the laws of gases to dissolved substances, together with Arrhenius' theory of dissociation, has shown us the probable molecular condition of many substances in solution. It has thus become often only necessary to determine the electrical conductivity of a solution, its freezing- or boiling-point, its vapor-pressure, or one of a number of other properties, to learn whether the solute is present as simple molecules, or as polymerized or dissociated molecules. The extent of this association or dissociation may also be calculated.

A large part of the recent literature on the subject of colloids is concerned with attempts to learn the condition of the dissolved substance by some of the methods referred to. This work may be briefly summarized by stating that in most cases the conditions under which the measurements were made only left open the alternative conclusions that there was no substance in solution in the sense that ordinary acids, bases and salts and many simple organic substances dissolve, or the dissolved substance was possessed of an exceedingly high molecular weight corresponding to an association or polymerization not easily understood.

Thus Sabanejew (30)[1] by means of freezing-point determinations is forced to attribute a molecular weight of over 100,000 to silicic acid in the hydrosol, while experiments by Gladstone and Hibbert (27) similarly lead to the conclusion that the molecular weights of ferric hydroxide and aluminum hydroxide in solution

[1] Such figures refer to the references at the end of this article.

exceed 5,000. It may be true that molecules of such magnitude exist in solution and that to them may be ascribed all the functions of simple dissolved molecules, but in the absence of proof that such is the case it will probably be more fruitful to follow the plan of several modern investigators (116, 49, 35,), and consider the colloid solutions as simple suspensions of otherwise insoluble material. With this in view the first step is naturally to compare so-called colloidal solutions with what are known to be simple suspensions or heterogeneous mixtures. If a hydrosol resembles a mixture of sand and water in which the sand, because of its degree of fineness, does not settle, then the two ought to have other common properties. Such is actually the case, and it may be truly said that the hydrosols possess only those properties which would naturally be ascribed to them if they were regarded as suspensions of finely divided insoluble substances.

It would be impracticable here to consider in detail the hundreds of different colloids thus far studied, but a cursory view of the methods of their production will call attention to the following general principle : when any substance is produced within a liquid in which it is insoluble, it will, at least temporarily, exist there in the so-called colloidal state ; but this colloidal state is rapidly destroyed by the presence of electrolytes.

A clearer idea of the value of what follows will be gained if one recognizes at this point the probable necessity of attributing electrostatic charges to particles of any kind when suspended in a liquid, and of assuming that these charges, while they may be positive or negative for different kinds of suspended matter, must still be of the same sign for all particles of the same substance. It is known that two different substances in contact assume equal and opposite electrostatic charges at their contact surfaces, and the work of Quincke, Coehn, and others has brought to light the regularities of this phenomenon.

Suspended particles of finely divided sulphur, silica, etc., in water, exhibit negative charges exactly as larger masses of the same substance in contact with water do, and when the suspension is placed between two electrodes connected with a source of electromotive force, the particles all migrate in the direction of the negative current. Conversely too, water in capillary tubes made of such materials as charge themselves negatively in contact with it, moves with the positive electricity through the capillary

under the influence of the electric current. Similarly, particles suspended in turpentine assume in most cases the opposite charge as compared with the water, and under influence of the electric current move in the opposite direction.

Coehn (99) was led to conclude that a substance having a higher dielectric constant than the liquid in which it is suspended assumes the positive charge, while if of lower dielectric constant its charge is negative. It is probable that this does not alone determine the nature of the charge, which at least in many cases must depend also on electrolytic solution pressure and the partition coefficient for the ions of dissolved electrolyte between the suspended material and the liquid (123).

We seem forced then to recognize electrostatic charges on suspended particles, and it seems just as necessary to accept the conclusion that, as a result of these charges, suspended particles, whose masses are small enough, are equally distributed throughout the liquid and prevented from ever coalescing or settling because of the mutual repulsion of these charges. This mutual repulsion might also cause measurable osmose and corresponding osmotic pressure, properties which the colloids have to a slight degree.

The following illustrates some of the relations between "sols" and suspensions, the various methods of producing colloidal solutions or hydrosols, and the fact that absence of electrolytes usually insures permanency of colloidal state.

If an aqueous solution of a silicate be treated with the equivalent quantity of an acid, free silicic acid and a salt are formed. This silicic acid is in the colloidal state, not in the form of a simple dissolved substance, and if the salt present is not very dilute, the acid becomes coagulated or exhibits its insolubility; *i. e.*, the particles of suspended acid collect together. If the electrolyte be removed by osmose or otherwise, or if the silicic acid be made by such a method that electrolytes do not remain in the solution, the hydrosol is stable. It may, however, be precipitated at any time by the addition of electrolytes. For example, stable silicic acid hydrosol may be made by treating silicon tetraethyl with water, the alcohol resulting not having any effect on the silicic acid. This remains in the "sol" condition indefinitely but is precipitated by any electrolyte (Grimaux 16). Bredig (83) has shown that a great many metals may be produced in the hydrosol state by simply

forming an electric arc under water between terminals of the metal desired. The heat of the arc volatilizes the metal and the vapors condense in the water, yielding deeply colored suspensions or colloidal solutions which often do not settle in measurable time, but which are immediately precipitated by even traces of most electrolytes and are not affected by non-electrolytes.

If arsenic or antimony sulphide be produced by the action of hydrogen sulphide on aqueous solutions of the oxides of these metals, there is at no time any considerable concentration of electrolytes present and there always results a deeply colored liquid, from which nothing is separated by ordinary filtration. Linder and Picton have studied these hydrosols and have shown that very low concentration of electrolytes completely precipitate them. Most other insoluble sulphides have been produced in the hydrosol state and have shown the same properties (Winnsinger 26).

Sulphur in the hydrosol state may also be produced by the mutual action of aqueous solutions of sulphur dioxide and hydrogen sulphide. The sulphur thus formed in the absence of electrolytes is in a stable, apparently soluble condition, from which it is precipitated by the presence of electrolytes (Stingl and Morawsky 12). Selenium also undergoes the same modification by analogous treatment (Schulze 19).

The hydroxides of many of the metals may be made as hydrosols by methods which involve the principle above stated. A solution of ferric hydroxide in aqueous ferric chloride solution, when subjected to osmose to remove most of the chloride, yields a colloidal hydroxide solution which is stable, but is precipitated by most electrolytes. Grimaux (16) has shown that by the reaction between ferric ethylate and an excess of water, stable ferric hydroxide hydrosol is produced. Here there are no electrolytes present like those which, in the usual metathetical reaction for the production of such compounds, cause a coagulation and precipitation of the insoluble substance. Other hydroxide hydrosols may be made in a similar manner.

A solution of one part of egg albumen in ten or more parts of pure water does not yield any visible insoluble matter on boiling, although the effect of the heat may well have produced the insoluble material which more concentrated albumen solution would yield when similarly treated. This solution of so-called

modified or alkali albumen is capable of coagulation or precipitation by electrolytes, although it is stable in their absence (Hardy 131, 132).

Several purely organic colloids have been synthetically produced by Grimaux (16) and by Pickering (69), but always in the absence of electrolytes; moreover electrolytes easily precipitate or coagulate them, while non-electrolytes do not. There are produced in nature, in growing plant and animal cells, many colloids which probably owe their precipitation or deposition to electrolytes; this fact makes the study of the properties of this class of bodies of the utmost importance to biology.

In the case of simple, well recognized suspensions of insoluble material, such as silica, clay, oil, etc., it has long been recognized that the settling or coagulation is produced or very greatly accelerated by electrolytes, while non-electrolytes have little or no effect. This principle is used in connection with stamp-mills, etc., for the precipitation of so-called slimes, and it is of interest to the geologist in that it accounts for the formation of the delta at a river's mouth, where the settling seems to be induced by salt water rather than by loss of current in the stream. It is a principle also applied in the purification of water supplies and sewage. It has been studied by Scheerer (3), Barus and Schneider (35), Spring (139), Stark (114), and many others.

In general, acids and the salts of heavy metals are most active in this coagulative effect on suspensions, the alkali salts having the power to a less marked degree, but the general property of electrolytes of precipitating such suspensions, even when the former is exceedingly dilute, is repeatedly discovered. Similarly, as shown in the methods of preparation, the hydrosols or colloidal solutions are capable of coagulation or precipitation by electrolytes and often by exceedingly minute quantities. The colloidal platinum described by Bredig (83) is often precipitated in a few hours by the impurities in ordinary distilled water, while in very pure water it is stable for months or years. Quantitative work on this precipitation will be described later. It may be said here, however, that in this respect there seems to be really no difference between ordinary suspensions and so-called hydrosols. The two classes, if indeed they are not identical, also have the common property of very slight diffusibility and of behaving alike when filtered through porous cells (133), parchment membranes, etc.,

and they practically, without exception, exhibit in a pencil of light the Tyndall phenomenon of diffusion of the ray. Its path through the liquid is visible and the reflected light of the ray is polarized.

Several investigators, among them Linder and Picton (80), Coehn (79), Spring (112), and Hardy (131), have shown that the colloidal material, in the hydrosol or so-called dissolved condition, migrates under the influence of the electric current and collects about one electrode, the direction of movement depending on the nature of the colloid. This is exactly what Quincke (5) and others have observed for visible particles in suspension under the same conditions.

Thus it seems most logical to consider so-called colloidal solutions as finely divided suspensions, the particles of which are much larger than simple molecules, the mixture being heterogeneous, instead of homogeneous, or consisting of two phases instead of one. This point has been very recently briefly discussed and a theory proposed by Donnan (147).

A number of investigators (Schulze, Linder and Picton, Hardy) have studied quantitatively the precipitation of the colloids by electrolytes, and very interesting results have been obtained. At least in the case of many of the colloids, the molecular concentration of the acid or salt required to produce coagulation is determined almost wholly by the valence of the positive ion, being independent of the nature of the negative ion and having nearly the same value for different positive ions of the same valence. The reciprocal of this concentration is designated the coagulating power of the electrolyte; and if its value for positive univalent ions be represented by 1, that of the bivalent ions becomes about 30 and that of the trivalent about 1000. Quantitative experiments by four different chemists on the sulphides of arsenic, antimony, and cadmium, on the hydroxide of manganese, and on boiled dilute egg albumen, have shown the above ratio to hold fairly well. This point may well be illustrated by examples: Colloidal antimony sulphide is precipitated by most of the univalent salts when the concentration is about 1 part by weight of salt to 200 parts of the solution; for the bivalent salts, this value is about 1 part by weight to 2,000 of water, while with the trivalent ions, 1 part of the salt to 30,000 or 40,000 of water is sufficient. Corresponding concentrations

of non-electrolytes are practically without effect. Another author states that sodium, potassium, and ammonium salts precipitate colloidal copper sulphide when 1 part by weight of the salt is present in from 60 to 400 parts by weight of water. Salts of the bivalent elements, when present, 1 part in from 3,000 to 7,000 parts of water and the trivalent salts in from 30,000 to 70,000 parts of water. Undissociated acids are without effect, while dissociated acids are about like univalent salts. For a certain arsenious sulphide solution, 1 part of potassium chloride to 137 parts of water is necessary; while with ferrous sulphate and similar salts, 1 part in 2000 or 3000 parts of water, and with ferric chloride 1 part in 50,000 parts of water suffices, the values for iron, chromium and aluminum in this case being 50,000, 83,000 and 20,000. As might be expected, the alums here act as trivalent-metal salts, while the ferrocyanide and ferricyanide of potassium act like other valent-metal salts. Experiments on suspended sulphur by one author, and on diluted, boiled egg albumen by another, have shown the same quantitative relations.

Several chemists have suggested possible explanations of these phenomena. It is thought by some recent investigators that the coagulating power of salts on aqueous suspensions and on many of the so-called colloids, is attributable to the positive or to the negative ion of the salt, depending on whether the suspended particles themselves are negatively or positively charged with respect to the solution; that is, that the negatively charged suspensions are precipitated by positively charged ions, and conversely. Spring (139) believes the statical charge, which it is assumed the ions of electrolytes carry, neutralizes the statical charges of opposite sign on colloidal particles, and cites cases which seem to support the belief. For example, he states that certain colloids are negative and therefore require for their immediate precipitation or coagulation a certain concentration of a positive ion. Solutions of various salts of the same cathion should therefore be equally active as precipitants when they are equivalent in concentration, while equivalent solutions of salts of the same anion should not be equally active. This he has shown to be the case. Whetham (121) has attempted to explain the observed relative coagulating or precipitating powers of ions is influenced by their valences as follows. He assumes that it is necessary that a certain

minimum electric charge, carried by the ions, must be brought within reach of the colloidal group with a certain minimum frequency throughout the solution in order to produce coagulation. Evidently equal charges should be available from $2n$ triad ions, $3n$ diads and $6n$ monads, where n is a whole number. Probability of contact between colloid and ion should be proportional to the concentration C of the ion or equal to AC, where A is a constant. The probability of two such ions being together is $\overline{AC}^{2}$ and of "n" ions $\overline{AC}^{n}$. For equal coagulative power of ions of different valences $\overline{AC_3}^{2n} = \overline{AC_2}^{3n} = \overline{AC_1}^{6n} = B$ (a constant). The concentration of trivalent, bivalent and univalent ions respectively being C_3, C_2, C_1, hence $C_1 : C_2 : C_3 = 1 : \sqrt[3]{B} : \sqrt[2]{B} = 1 : K : K^2$, where K is a constant. That is, from the known coagulating powers of univalent and bivalent ions, that of ions of higher valencies could be calculated. The calculated and observed values for trivalent ions thus far investigated agree very satisfactorily. Measurements with quadrivalent ions have not been made.

Whetham supposes a certain minimum charge has to be brought into contact with the colloid particles with a certain minimum frequency throughout the solution. We see no reason for assuming a certain minimum frequency. On the contrary it is more probable that whenever contact between any colloid particle and a certain necessary minimum amount of electric charge takes place, coagulation of that particle results, and that the frequency of contact simply determines the rapidity of coagulation of the solution as a whole. Evidently then, we might have various concentrations of the same electrolyte, all of which precipitated the colloid completely, but after expiration of different times. This velocity would then be a function of the concentration and for immediate precipitation the relationships might hold, as shown by Whetham. It is a well-known fact that with all the colloids the velocity of coagulation or precipitation may assume any desired magnitude depending on the concentration of precipitating agent. The many comparisons of the coagulating power of different electrolytes for immediate coagulation led to the discovery probably first stated by Schulze, but confirmed by Linder and Picton and others, that ions of the same valence have only approximately the same precipitating or coagulating power, while for different valence the

power is greatly different as stated above. Spring has added the velocity of migration of the ion as a factor in determining its precipitating power because of the fact observed by him that potassium, sodium, and hydrogen in this respect stand in the order of their migration rates. Such a dependence is to be expected if the assumption of Whetham is a correct one. In this connection it is interesting to note that Linder and Picton have observed, apparently, a peculiar class of analogous phenomena in the case of colloidal aniline colors. They mixed solutions of aniline colors which migrate in opposite direction under the influence of the current and whose particles under our present hypothesis are possessed of opposite electric charges, and report that "in general there is a tendency to aggregation between such substances." The mixed solution was either completely precipitated or the particles simply increased in size; just such effects as are produced by electrolytes in large and small quantities respectively. Thus, aniline blue (—) and methyl violet (+) mix in this way, and, unless very dilute, precipitate; and even when dilute, optical tests show that the particles have increased in size. Aniline blue (—) and magdala red (+) give similar results. In dilute solutions, to show that some union had taken place, the authors filtered the mixture through a porous cell, which held back both in case of the mixture, while aniline blue would filter through when tested separately. Rosaniline hydrochloride and aniline blue acted similarly. Here, as Linder and Picton state, we have what appears to be "a mimicry of the ionic dissociation," but is there any reason why it may not be a true conception of the actually occurring phenomena?

Finally, it must be mentioned that Linder and Picton have stated that when a colloidal solution, or, as they designate it, a pseudo solution, of arsenious sulphide, is precipitated by a salt such as barium chloride, a small portion of the barium is precipitated along with the sulphide, while the corresponding quantity of the negative element, chlorine, is not, and that this barium cannot be removed from the precipitate by washing with water. It can, however, be replaced by another positive ion by washing with a solution of an appropriate salt.

PART II.

EXPERIMENTS ON THE CO-PRECIPITATION OF THE ELECTROLYTE WITH THE COLLOID.

The results of Linder and Picton, which have just been referred to, seemed to us to open a field of great scientific interest, and one likely to become of much practical importance to the analyst, in connection with the carrying down and retaining of otherwise soluble materials by precipitates. In order to confirm and extend these results, our investigation was undertaken. A colloidal arsenious sulphide solution was made by pouring a solution of Merck's C. P. arsenious oxide, a little at a time, into an excess of a saturated aqueous solution of hydrogen sulphide, so that the resulting solution contained about 1 per cent. arsenious sulphide. The excess of hydrogen sulphide was then removed by passing washed hydrogen through the mixture. There resulted a deep lemon-yellow solution which was opaque by reflected light but transparent by transmitted light, and which, except for a practically unweighable quantity of precipitated sulphide, passed readily through the best filter-paper. It also showed no signs of heterogeneity under the microscope. The water used in these experiments was twice distilled, the second time from alkaline permanganate solution, and was such as is usually employed in electrical conductivity measurements. An approximately 1 per cent. solution of barium chloride was made by dissolving the crystallized salt in water. Thirty cc. of this solution were added to 200 cc. of the colloidal solution, which produced immediate and complete precipitation of the arsenious sulphide. This was filtered and carefully washed until the washings gave no test for chlorine with silver nitrate. The barium in the filtrate and wash-water was then precipitated as sulphate and weighed, and at the same time a determination of the barium in 30 cc. of the original barium chloride solution used was likewise made. The weights of sulphate obtained were 0.2590 and 0.2849 gram respectively, which correspond to 0.1523 and 0.1675 gram of barium; or a loss of 0.0152 gram of barium which was held by the precipitated sulphide. The analysis of the filtrate from the arsenious sulphide precipitate for chlorine by weighing silver chloride showed 0.0863 gram as compared with 0.0865 gram found in the same way in 30 cc. of the barium chloride solution used.

This shows that the chlorine was not carried down with the sulphide to a measurable extent.

To determine the effect of concentration of the colloid on this phenomenon, half as much, or 100 cc., was taken and diluted to 200 cc., the volume used above. Thirty cubic centimeters of the barium chloride solution as before were added to this and the analysis made as above. It was found that 0.0078 gram of barium had been carried down by the sulphide. Finally 100 cc. of the colloid solution, 80 cc. of water, and 50 cc. of the barium chloride were mixed and the process carried out as before. The barium held by the sulphide was here 0.0075 gram. As these are practically half of the previous quantity (0.0152), it is evident that *the composition of the precipitated colloid is independent both of its own concentration in the solution and of that of the barium ions.* The approximate relationship in the precipitate is represented by the symbol $90(As_2S_3) : Ba$. It is doubtless true that the barium exists here as hydroxide as will be shown below. That the barium remained adhering to the sulphide, was shown by the following experiment, which is a repetition of Linder and Picton's procedure. 100 cc. of the colloid solution were diluted with 100 cc. of water and coagulated with 30 cc. of the barium chloride solution. The precipitate was washed free from chloride and then allowed to stand in dilute ammonium chloride solution for two days. The precipitate was again filtered and the barium in the ammonium chloride solution determined as sulphate. Thus 0.0071 gram of barium was found, which was 93 per cent. of that carried down by the sulphide (0.0076 gram). This had been removed from the washed sulphide by the ammonium chloride solution. This is in accord with Linder and Picton's statement that the metal carried down by the arsenious sulphide can be replaced by other metals by digesting as above.

The natural assumption to make in the light of these experiments is that the colloid causes hydrolysis of the salt and that while the base is carried down in the precipitate, the filtrate contains the free acid. How this precipitation of a basic hydroxide can be produced, together with the liberation of the acid, is yet to be explained. That the filtrate in the above experiments did contain free acid after the process, while it did not before, was readily shown, and the quantity which was found by titration with alkali agreed with the assumption. For example,

in cases where, as above, 200 and 100 cc. of the colloid had been used, the free acid in the filtrate was found to be equivalent to 0.0081 and 0.0038 gram of chlorine respectively. The very dilute solutions made the determination difficult; but these values correspond quite well with the results in the case of the barium carried down which require 0.0079 and 0.0039 gram respectively. Therefore, *equivalent quantities of barium and hydroxyl are precipitated with the colloid.*

This power of what one might consider chemically inert material, by virtue of which it decomposes neutral salts in the presence of water and combines with or holds either the acid or base, has already been discovered in the case of solid substances, especially porous material such as bone-black, silica, precipitated colloids, and has received very interesting treatment by Van Bemmelen (141). In the case of solids, however, quantitative measurements seem hardly destined to lead to such interesting results as are promised by a study of what appears to be the same phenomenon in colloidal solutions.

The experiments above described have been repeated, using strontium, calcium, and potassium chlorides instead of barium chloride, and the following results which are tabulated below, together with those given above, were obtained. The calcium was precipitated as oxalate and weighed as oxide. The strontium was weighed as carbonate and the potassium as potassium platinichloride. In the first column is given the amount of the colloidal solution used, in the second the quantity of water added, in the third the volume of the precipitant used, in the fourth the weight of the metal in the precipitant used, in the fifth the weight of this metal carried down by the precipitate, in the sixth the weight of chlorine found in the filtrate as free acid, and in the seventh the weight of chlorine corresponding to the metal in the fifth column.

CALCIUM CHLORIDE.

Colloid solution. cc.	Water. cc.	Precipitant. cc.	Metal in solution. Gram.	Metal in precipitate. Gram.	Chlorine as free acid. Gram.	Chlorine calculated from metal. Gram.
100	100	25	0.0724	0.0020	0.0036	0.0036
200	...	25	0.0724	0.0038	0.0073	0.0067
100	100	25	0.0724	....	0.0041	0.0036
			STRONTIUM CHLORIDE.			
200	...	25	0.1071	0.0072	....	....
200	...	25	0.1071	0.0083	....	....
100	100	25	0.1071	....	0.0040	....

BARIUM CHLORIDE.

Colloid solution. cc.	Water. cc.	Preciptant. cc.	Metal in solution. Gram.	Metal in precipitate. Gram.	Chlorine as free acid. Gram.	Chlorine calculated from metal. Gram.
200	...	30	0.1675	0.0152	0.0081	0.0079
100	100	30	0.1675	0.0078	0.0038	0.0039
100	80	50	0.2791	0.0075	....	....

POTASSIUM CHLORIDE.

100	...	..	2.0	0.0032	0.0030	0.0029
200	...	..	5.0	....	0.0073	....

The quantities of these various metals carried down by 100 cc. of the colloid are calculated and collected in the following table. The third column contains the quantities of the respective elements chemically equivalent to the barium absorbed. This element is chosen on which to base a comparison, because its quantitative determination is probably the most accurate.

I.	II. Grams observed.	III. Grams calculated.
Ca	{ 0.0019 { 0.0020	0.0022
Sr	{ 0.0036 { 0.0041	0.0049
Ba	0.0076	0.0076
K	0.0036	0.0043

In the case of another solution of the colloid which contained 19 grams of arsenic trisulphide per liter, the following results were obtained:

Colloid solution. cc.	25 cc. chloride solution.	Metal in solution. Gram.	Chlorine as acid. Gram.
50	Ba	0.1394	0.0019
50	Ba	0.1394	0.0021
50	Ca	0.0706	.....
50	Ca	0.0706	.....
50	Ca	0.0706	0.0017
50	Sr	0.1071	0.0021
50	K	2.00	0.0021
100	Ba	0.1394	0.0039
100	Ba	0.1394	0.0039
100	Sr	0.1071	0.0042
100	Ca	0.0706	0.0041
100	Ca	0.0706	0.0040
100	K	2.00	0.0038

The determinations of the quantity of metal carried down by the precipitate were not made in these experiments as the time at our disposal would not permit it. The analysis of the filtrate for fere acid was considered a measure of the quantity of metal car-

ried down by the precipitate as it proved itself to be in the previous experiments where both were determined.

Therefore, since the quantities of free acid were found to be the same, within the limits of error, in all the experiments, it is evident that equivalent quantities of the four metals were precipitated with the colloid. Thus, not only does this colloid, when precipitated, bring about a hydrolysis of the salts, absorb the base, and liberate the acid, but, what is equally striking, it carries down with itself chemically equivalent quantities of the different bases. In other words, *into this precipitated colloid, barium, strontium, calcium, and potassium enter in the proportions of their equivalent weights.* It is evident that this result supports the hypothesis of Whetham (see above).

PART III.

AN INDEX TO THE LITERATURE OF COLLOIDS.

The accompanying list of references is a fairly complete one and includes some articles which are only indirectly connected with the subject. To facilitate its use, the matter treated in the article is briefly stated, we having taken the liberty of substituting in many cases descriptive clauses for the titles given the papers by the respective authors. Owing to the necessary brevity of these modified descriptions, much very important material contained in many of the articles is still not specially referred to, but it was thought that even these brief descriptions might facilitate the use of this collected literature.

REFERENCES TO COLLOIDS.

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NOTE.

Reply to Dr. Ewell's "Notes on the Paper by Hiltner and Thatcher.—In an article recently published in this Journal, we outlined a modification of the Sachs-Le Docte modification of Pellet's "instantaneous aqueous diffusion methods for the estimation of the sugar content of beets." In the succeeding number of the Journal, Dr. E. E. Ewell published some notes on our paper[1] criticizing the proposed modification in several points. Inasmuch as Dr. Ewell has apparently fallen into some of the errors which we specifically warned against in our previous article, it would seem that a further word of comment is necessary. This reply has been delayed by the withdrawal of Mr. Thatcher from this laboratory and by the many distractions of the summer vacation season, but may not be out of place at this time.

[1] This Journal, 23, 432.

The object for which the work reported in our previous article was undertaken, was an investigation of the possibility and feasibility of doing away with the necessity of weighing an exact definite weight of beet pulp for each analysis, and using instead any known weight of pulp with its proportionate amount of water and lead subacetate solution. When we began the work we were unaware that such a device had ever been suggested, since Walawski's work had not yet been published in any of the journals on file in our library. Subsequent correspondence with the Division of Chemistry at Washington, secured for us a copy of a translation of the paper of Dr. Sachs from which we quoted freely in our article. After we had completed our work and a copy of the report of it had gone into the hands of the printer, a personal letter from Dr. G. L. Spencer informed us that he had for some time past been making use of a modification of the method in question, by which any desired weight of pulp might be proportionately diluted, clarified, and polarized. The idea, although original with ourselves, was therefore not new, but inasmuch as our modification differed in some essentials from the commonly adopted methods, and in some important respects from Walawski's process, particularly as to practical details—its publication was considered advisable.

Dr. Ewell criticizes the suggested modification because it is based upon a correction for the volume of water in the beet rather than the volume of juice, or liquid in the beet. It is admitted at the outset, of course, that either the Sachs-Le Docte assumption of an average juice factor or our assumption of an average water factor will give results varying somewhat from the truth in individual cases. Which of these two assumptions is the more desirable as a basis for a rapid method for technical analysis depends, therefore, upon two things: first, the probable error that may be introduced in individual analysis, and, second, the ease with which a factor to accurately represent the average of the beet to be analyzed may be determined.

Researches during the past ten years by sugar-house and experiment-station chemists show that the amount of *marc*, or insoluble matter, in the beet often rises to 8 per cent. and sometimes even to 10 per cent. of the weight of the beet. A very large number of direct determinations of this factor made at this laboratory during the past seven years shows that in immature or

low-grade beets, it sometimes falls as low as 2 per cent. This is shown in the following table:

TABLE I. INSOLUBLE MATTER (MARC) IN BEETS.

Year.	Number of determination.	Maximum. Per cent.	Minimum. Per cent.	Average. Per cent.
1892	15	8.4	2.5	4.1
1894	6	4.6	2.2	3.3
1895	14	7.0	2.4	3.7
1896	7	3.6	2.0	2.4
1897	10	5.9	2.2	3.5
1898	8	4.0	2.0	2.9

Hence the assumption of 5 per cent. of insoluble solids, or 95 per cent. of juice, as an average for the calculation of the volume occupied by this juice must produce a significant error in many cases. The tediousness and extreme difficulty of a direct determination of the amount of insoluble matter in beets, and the unreliability of the results obtained by an indirect estimation of this factor, make it almost impossible to control the work of any given season or portion of a season by a determination of the correct average juice factor of the beets to be analyzed.

Furthermore, the calculation of the volume occupied by a definite weight of juice by the ordinary methods is subject to several errors. In the first place the usual method of determining the specific gravity of the juice by means of the Brix spindle gives erroneous results because the spindle is calibrated in solutions of pure sugar. Investigations carried on in this laboratory through several seasons show that the results obtained in this way are almost invariably too high, the percentage of total solids obtained by a direct determination, or indicated by an accurate determination of the specific gravity of the juice, being always less than that indicated by the spindle. As is shown in the following table, the real coefficient of purity is always higher than that obtained by calculation from the Brix spindle and polariscope readings. In other words, the amount of non-sugars in solution is less than that generally accepted and the volume of the resulting solution is, therefore, less.

TABLE II. REAL VERSUS APPARENT PURITY.

Year.	Number of determinations.	Differences between real and apparent purity. Maximum difference. Per cent.	Minimum difference. Per cent.	Average difference. Per cent.
1892	13	+ 9.10	+ 3.30	+ 6.2
1894	6	+ 6.30	+ 3.30	+ 4.6
1895	15	+ 9.13	+ 2.96	+ 5.2
1896	10	+ 5.97	+ 1.20	+ 3.4
1897	14	+ 5.97	+ 2.34	+ 3.8
1898	9	+ 4.80	+ 1.70	+ 3.3

It is evident, then, that the only correct basis from which to calculate the volume of any given weight of juice is a direct determination of the specific gravity of the juice, or of the total solids in solution in it. This latter is the same determination upon which we base our correction for water content.

Again, even though the volume of the juice in the sample taken be correctly determined, the figures are of no real value in determining the volume of water to be added, since the juice is clarified by the same process by which its volume is to be increased to the *normal* dilution, the percentage of solids in solution being materially diminished with its attendant effect upon the volume of the solution. A portion of the soluble non-sugars as well as a portion of the lead in the clarifying agent are removed from the solution by precipitation. The exact amount of the diminution in volume due to this cause in any particular case it is impossible to determine. It is obvious, however, that Dr. Ewell's carefully prepared tables, based upon the assumption that the juice in the pulp taken has the same specific gravity as would a solution which contained a percentage of pure sugar, equal to the apparent amount of total solids in the juice, and that the solution contains all the solids originally present in its constituents are not true to facts and lead to erroneous conclusions. Moreover, both of the errors introduced are such as would, in actual practice, tend to diminish the total volume of the solution and so in part, counteract the error due to the increase in volume caused by the sugar dissolved on the water of the juice.

It would seem, therefore, that both the theoretical consideration of the matter and the practical results obtained, and reported in our previous article, show that the assumption of an average water factor as a basis for a rapid working method is fully as satisfactory as that of an average juice content. The determination of the correct average factor to be used in any series of analyses is unquestionably much more easily made in the former case. The error in individual cases might be lessened by doubling the dilution as required by the Sachs-LeDocte modification, but as was pointed out in the previous article (see page 310), this has not been found necessary in ordinary work.

Dr. Ewell further criticizes our work "because their determinations of the water contained in beets, * * * are higher than is indicated by previous results or determinations of the amount of

filter contained in beets" and further states "that as little as 4 per cent. of marc is possible, but 2.61 per cent. is doubtful and 2.28 per cent. is still more so" and supports his criticism by tables calculated from assumed conditions. The figures cited in Table I above are sufficient to show that the results recorded are not at all impossible, but, on the contrary accord very satisfactorily with the other observed facts concerning the beets with which we had to deal. The results which we have recorded on pages 308 and 309 in every case were those obtained by the best of the direct methods of determination and not by indirect calculations using arbitrary factors. It is but fair to add that, owing to very late warm Fall rains in Nebraska last year, the beets which were available for work at that time were very largely immature and unripe ones. It is hoped that in the near future, the applicability of the proposed method may be further tested on a better class of beets. The determinations of moisture recorded on page 309 of the original article were made on beets at all stages of growth from samples taken from July 15th to November 15th of each year, and, hence, as was stated, represent widely varying conditions of the beet.

It is a fact well known among chemists actively engaged in work with beets that the factors arbitrarily adopted to represent an average beet are often far from the real conditions to be met with in actual work and that percentages calculated from these arbitrarily assumed standards are by no means sufficiently reliable to afford a basis for criticism of results obtained in actual practice.

Our critic makes a number of logical deductions from certain computations that he has made, but we must beg to insist that he errs considerably in his premises. As a basis for his calculations on page 433 he makes an assumption as to purity coefficient (80 per cent.) which is quite untenable in view of the facts as ascertained by us. The coefficients of purity of the beets in question seldom reached 75 per cent., as our records show; many analyses indicated a purity of less than 70 per cent., some indeed as low as 65 per cent. Were we to apply such factors as these in the same manner as Mr. Ewell has applied the factor 80 we would obtain most astounding figures. The danger in building too much on averages and on conventional factors is here very apparent.

Although a little remote from the main point in question we

wish finally to notice the fact that in making these computations for the tables on page 433, errors have been made aside from those just mentioned. The values there used, for average sugar content in the beets, were obtained by us by indirect analysis of the beets. The percentages of sugar in the juices were first determined and from these the percentages in the beets were estimated by deducting the conventional 5 per cent. for marc. Using these same figures in connection with other data, Mr. Ewell *calculates* the percentages of marc to range from 1.79 per cent. to 4.74 per cent. The error also in attempting to calculate *soluble non-sugars in the beet* and later the percentage of marc by employing an assumed factor (or even a definitely determined factor) of *purity of the juice* is quite apparent. (By factor of purity of the juice we mean, of course, the ratio of sugar in the juice to soluble total solids in the juice; and by soluble non-sugars the difference between total solids and sugar in the juice.) By thus confusing the values for the beet and those for the juice it is manifestly impossible to compute values for marc or other components of the root.

To conclude, we wish only to again draw attention to the facts stated on page 311, *et seq.*, of the current volume of this journal regarding the experimental part of our work and especially to Table III. where the results obtained by the proposed method are compared with those secured by Pellet's hot aqueous diffusion process (an acknowledged standard method). The results given certainly point plainly to the reliability of the method and indicate that the process is based on correct principles.

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